ChemPubSoc Europe

DOI: 10.1002/ejoc.201901622

EurJOC European Journal of Organic Chemistry
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Betaine–N-Heterocyclic Carbene Interconversions of Quinazolin-4-One Imidazolium Mesomeric Betaines. Sulfur, Selenium, and Borane Adduct Formation

Sergey Deev,*[a] Sviatoslav Batsyts,[b] Ekaterina Sheina,[a] Tatyana S. Shestakova,[a] Igor Khalimbadzha,[a] Mikhail A. Kiskin,[c] Valery Charushin,[a,d] Oleg Chupakhin,[a,d] Alexander S. Paramonov,[e] Zakhar O. Shenkarev,[e] Jan C. Namyslo,[b] and Andreas Schmidt*[b]

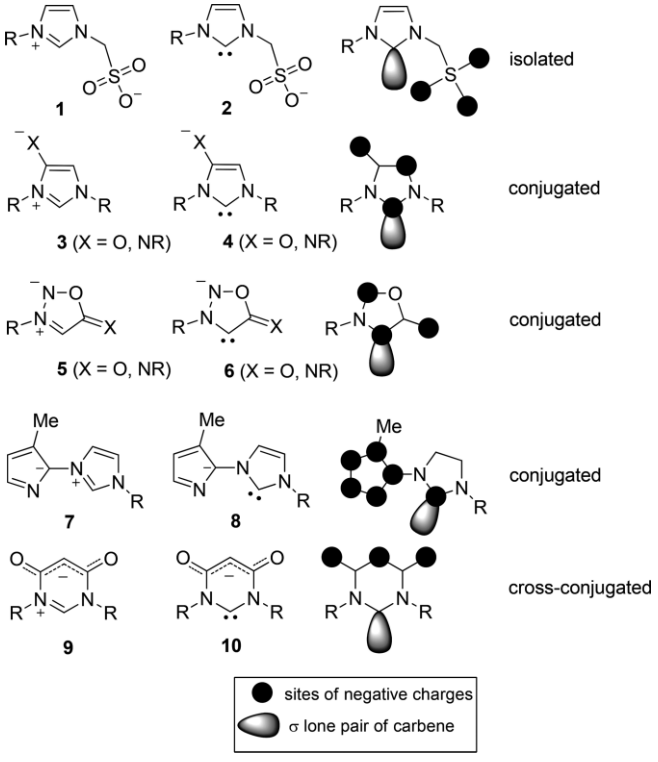
Abstract: Reaction of N-alkylated imidazoles with 2-chloro-4-quinazolinone gave mesomeric betaines, 2-(1-alkyl-1*H*-imidazolium-3-yl)quinazolin-4-olates, for which three tautomeric forms of *N*-heterocyclic carbenes (NHCs) can be formulated, in addition to an anionic NHC after deprotonation. The NHC tautomers were trapped with sulfur, selenium, triethylborane, and triphenylborane as thiones, selenones and borane adducts, respectively. We obtained two isomers of the cyclic borane adducts, diazaboroloquinazolinones with [1,5-*a*] and [5,1-*b*]-type fusion between the quinazolinone and the diazaborole rings. They correspond to two different NHC tautomers and to the anionic NHC derived thereof. The third NHC tautomer was trapped as a non-cyclic adduct with tris(pentafluorophenyl)-borane by coordination to the quinazoline oxygen atom. 2D ^{1}H-^{15}N HMBC experiments of ^{15}N-labeled quinazolinone fragments, quantitative measurements of long-range ^{1}H-^{15}N coupling constants (J_{HN}), and five X-ray single crystal analyses have been carried out for the structure elucidations and to gain insight into the NMR spectroscopic properties of these compounds.

1. Introduction

Since the first isolation of a stable N-heterocyclic carbene (NHC) by Arduengo in 1991,[1] this class of compounds has developed considerably and nowadays NHCs are ubiquitous in organic as well as inorganic chemistry. They are widely applied in catalysis, organocatalysis, and complex chemistry. The significance of N-heterocyclic carbenes and of their anionic derivatives is impressively demonstrated by numerous books,[2] monographs,[3] and review articles,[4] the latest of which reflect the broad applicability of this class of compounds. They deal with main group element adducts,[5] NHCs in materials chemistry,[6] NHCs as ligands in cross-couplings[7] and in rhodium-catalyzed reactions[8] as well as copper, nickel, and cobalt complexes.[9] The enhancement of the σ-donating properties of N-heterocyclic carbenes was one of the initial goals of the design of a broad variety of interesting structures, resulting in strong donors such as cyclic alkyl amino carbenes (CAACs)[10] and others. However, strong NHC donation can also have divergent effects in transition-metal catalysis.[11] It has also been shown that the properties of N-heterocyclic carbenes as well as of their anionic derivatives are not only governed by the donicity of their characteristic σ-lone pair and the σ-framework of the parent heterocycle, but also by their π-electronic architecture. As a result, the carbene properties depend significantly on the type of conjugation in the NHC framework.[12] For example, the negative charge of the anionic N-heterocyclic carbene **2**[13] (Scheme 1) derived from zwitterion **1** is not delocalized in terms of resonance. It can be classified as *isolated* anionic N-heterocyclic carbene. By contrast, the mesomeric betaines **3** and the corresponding NHC **4** (imidazol-2-yliden-4-olates, X = O[14] and imidazol-2-yliden-4-aminides, X = NR[15]) delocalize their negative charges within the π-electron system. The same is true for the sydnone carbenes **6** (X = O)[16] and their sydnone imine derivatives (X = NR)[17] generated from mesoionic precursors **5**, as well as for the ylide carbenes possessing the partial structure **8** derived from ylides **7**.[18] All anionic N-heterocyclic carbenes obtained

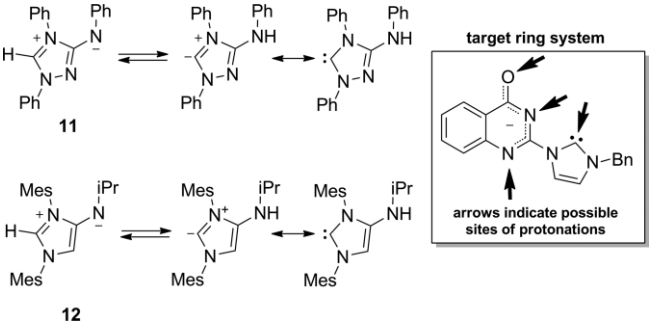
[a] *Ural Federal University, 19 Mira Street, 620002 Yekaterinburg, Russia E-mail: deevsl@yandex.ru*
[b] *Clausthal University of Technology, Institute of Organic Chemistry, Leibnizstrasse 6, 38678 Clausthal-Zellerfeld, Germany E-mail: schmidt@ioc.tu-clausthal.de https://www.ioc.tu-clausthal.de*
[c] *N. S. Kurnakov Institute of General and Inorganic Chemistry, RAS, 31 Leninsky Av., 119991 Moscow, Russia*
[d] *E I. Ya. Postovsky Institute of Organic Synthesis, Ural Branch of the Russian Academy of Sciences, 22 S. Kovalevskoy Street, 620219 Yekaterinburg, Russia E-mail: chupakhin@ios.uran.ru*
[e] *Shemyakin-Ovchinnikov Institute of Bioorganic Chemistry, Russian Academy of Sciences, 16/10 Miklukho-Maklaya Street, 117997 Moscow, Russia*
Supporting information and ORCID(s) from the author(s) for this article are available on the WWW under https://doi.org/10.1002/ejoc.201901622.

by formal deprotonation from these mesomeric betaines possess conjugated π-electronic backbones with delocalized negative charges which can be located on the carbene carbon atom itself according to the rules of resonance. Consequently, considerable atomic orbital coefficients of the highest occupied molecular orbitals (HOMO) are localized on these positions. Thus, the π-acceptor properties of the carbene carbon atoms are expected to change considerably in comparison to the reference imidazol-2-ylidene system. By contrast, the NHC **10**[19] derived from mesomeric betaine **9**[20] is cross-conjugated, as its anionic partial structure is π-electronically separated from the carbene center. Therefore the influence of the π-electronic backbone is considerably diminished in comparison to conjugated systems. The influence of substituent, field and resonance effects on the ease of N-heterocyclic carbene formation from imidazolium rings[21] and a quantitative analysis of factors influencing the ease of formation as well as the σ-bonding strength of selected oxa- and thia-N-heterocyclic carbenes[22] have been calculated and thus give an additional impetus for further progress in this field of chemistry.



Scheme 1. Examples of a zwitterion (**1**) and of mesomeric betaines (**3**, **5**, **7**, **9**) as well as their N-heterocyclic carbenes.

Apart from deprotonations, decarboxylations of pseudo-cross-conjugated mesomeric betaines such as heteroarenium-2-carboxylates to form pyridin-2-ylidenes,[23] imidazol-2-ylidenes,[24] pyrazol-3-ylidenes,[25] and indazol-3-ylidenes,[26] or tautomerizations of mesomeric betaines are efficient approaches to generate N-heterocyclic carbenes in situ. Thus, the reagent Nitron **11** has been identified as *crypto*-NHC as it forms metal complexes as well as sulfur adducts from its formal NHC tautomer (Scheme 2).[27] Analogous results have been achieved for the case of the imidazolium-aminide **12**.[15] In continuation of our interest in mesomeric betaines, N-heterocyclic carbenes and the intersection of these two classes of compounds,[28] we became interested in the quinazolinone core not only because of its biological significance (alkaloids,[29] cancerostatic,[30] sedative,[31] antifungal properties[32]) and applicability (e.g. as fluorescent dyes[33]) but also because it enables the formation of three different tautomers of its N-heterocyclic carbenes when a suitable heteroarenium ring such as imidazolium is attached. Therefore, we targeted at 4-quinazolinon-2-yl-imidazolium to gain additional knowledge about cross-conjugated systems. Its anionic NHC with possible sites of protonations is shown in Scheme 2.



Scheme 2. Tautomerizations of mesomeric betaines to give N-heterocyclic carbenes.

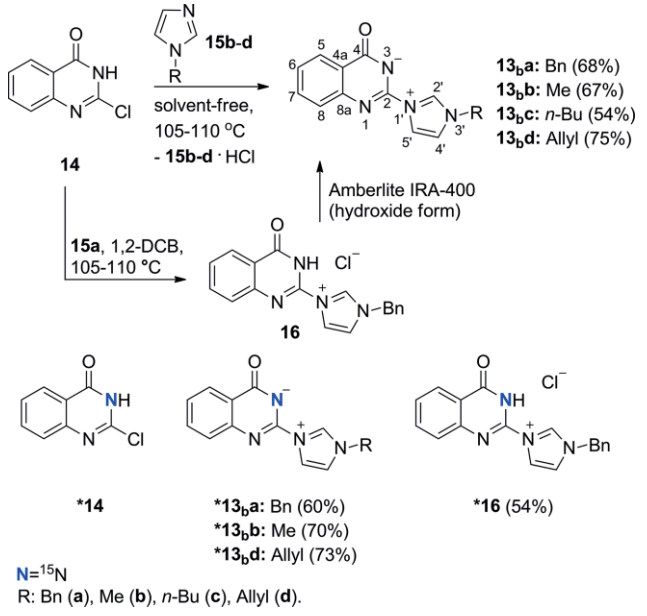
Herein, we report on the syntheses of our target ring system and carbene trapping reactions with sulfur, selenium, triethylborane and triphenylborane. σ-Donicities as well as π-properties have been estimated by means of $^{1}J_{CSe}$ and $^{1}J_{CH}$ coupling constants and ^{77}Se NMR chemical shifts. For structure elucidations of the boron adducts we used a new approach based on the analysis of long-range J_{HN}-couplings in 2D ^{1}H-^{15}N spectra of ^{15}N-labeled samples. To the best of our knowledge, the boron adducts are the first representatives of new heterocyclic ring systems.

2. Results and Discussion

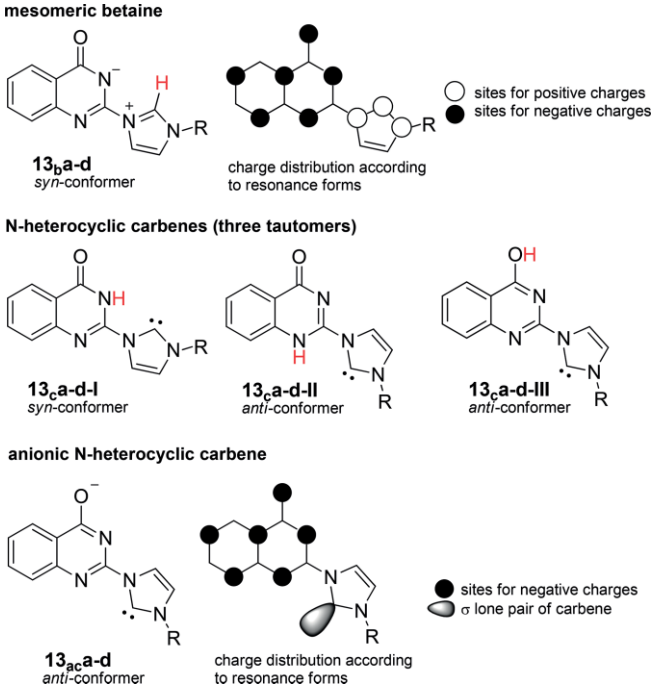
2.1. Syntheses

The syntheses of the target molecules was smoothly accomplished by C–N bond formation between 2-chloroquinazolin-4-one **14** and the N-alkylated imidazole derivatives **15a**–**d** (Scheme 3). Imidazole **15a** was dissolved in 1,2-dichlorobenzene (1,2-DCB), whereas all liquid azoles **15b**–**d** reacted without additional solvent. In the latter cases the mesomeric betaines **13$_b$b**–**d** were formed in one step, whereas **15a** gave the salt **16** which was converted into the betaine **13$_b$a** by the anion exchange resin Amberlite IRA-400 in its hydroxide form (the index "**b**" stands for "mesomeric betaine"). On treatment of the ^{15}N-enriched chloroquinazolinone ***14** (^{15}N, 95 %) with the imidazoles **15a**,**b**,**d** the labeled salt ***16** and the betaines ***13$_b$b**,**d** were obtained, and ***16** was then converted into ***13$_b$a** in analogy to **16**. Details of the synthesis of ***14** starting from 1*H*-benzo[*d*][1,3]oxazine-2,4-dione and ^{15}N-ammonium chloride (^{15}N, 95 %) are given in the Supporting Information. The ^{1}H

NMR signal of H2′$_{imidazole}$ is diagnostic for the betaine formation, as **16**/*16 showed a signal at 10.31 ppm, whereas the corresponding signals of the betaines **13$_b$a–d**/*13$_b$a–c were detected between 10.14 ppm and 9.88 ppm in [D$_6$]DMSO, respectively. No traces of the carbene tautomers **13$_c$a–d**/*13$_c$a–c (see Scheme 4) were detectable under these conditions (the index "**c**" stands for "N-heterocyclic carbene"). The selective incorporation of a ^{15}N label into the N3 position of the quinazoline fragment of the mesomeric betaines *13$_b$a,b,d were confirmed by a characteristic pattern of ^{13}C-^{15}N3 coupling constants ($J_{C\text{-}N3}$) and by 1D ^{15}N NMR spectra (see Table S1 and Fig. S2, Supporting Information). The long-range ^{1}H-^{15}N couplings (J_{HN}) with ^{15}N labeled and unlabeled nitrogen atoms (at natural ^{15}N abundance) were detected in the 2D ^{1}H-^{15}N HMBC NMR spectra, so that we were able to unambiguously assign all signals of the betaines **13$_b$a–d**/*13$_b$a,b,d to their corresponding nitrogen atoms. The ^{15}N1 and ^{15}N3 resonances were observed in the spectral ranges of 199–203 ppm and 208–216 ppm, respectively (see Table S2 and 2D ^{1}H-^{15}N spectra, Supporting Information).



Scheme 3. Synthesis of the target betaines; ^{15}N-labeled atoms are marked in blue. Numbering. The index "**b**" stands for "mesomeric betaine".



Scheme 4. Betaine, NHC tautomers and anionic NHC of **13**.

2.2. Classification and Calculations of the Betaines and Carbenes

The mesomeric betaines **13$_b$a–d** belong to the class of cross-conjugated mesomeric betaines (CCMB), as the resonance forms show no common atoms for either charge within the common π-electron system[34] (Scheme 4). Four different tautomers of **13$_b$a–d** can be formulated, three of which are the N-heterocyclic carbenes **13$_c$a–d-I–III**. The most stable conformers of **13$_b$b** and **13$_c$b-I** were calculated to be the *syn*-conformers as shown (ΔE = 3.6 and 54.5 kJ mol^{-1}, respectively), whereas the *anti*-conformers are more stable for the case of the tautomers **13$_c$b-II** and **13$_c$b-III** (ΔE = 68.3 and only 0.3 kJ mol^{-1}, respectively) according to DFT calculations (PBE0, 6-31G*). Among these tautomers, the betaine tautomer **13$_b$b** is the most stable, followed by NHC tautomer **I** (ΔE = 8.7 kJ mol^{-1}). The anionic N-heterocyclic carbenes **13$_{ac}$a–d** constitute the deprotonated form of the aforementioned species (the index "**ac**" stands for "anionic N-heterocyclic carbene"). They delocalize their negative charge exclusively within the quinazolinonide moiety according to the rules of resonance. The *anti*-conformer of **13$_{ac}$b** was found to be 7.8 kJ mol^{-1} more stable than its *syn*-conformer in vacuo.

The J_{HC} coupling constants of carbene precursors **13$_b$a–d** can be taken as a measure of the σ-donor strength of the corresponding NHCs.[35] We measured $J_{H2'\text{-}C2'}$ coupling constants between 225.7 Hz (**13$_b$c**) and 226.3 Hz (**13$_b$a**) (Table S3 and Fig. S3, Supporting Information) which resemble the value of 1,3-dimesitylimidazol-2-ylidene ($J_{H2'\text{-}C2'}$ = 225 Hz). A comparison between **13$_b$a–d** and the salt **16** can rule out contributions of intramolecular hydrogen bonds between C2′H and N3 in solution which might cause slightly increased values for the $^{1}J_{H2'\text{-}C2'}$ coupling constants,[36] as the values of the betaines and the salt are very similar. Thus, a coupling constant of 227.5 Hz was detected in **16**, which cannot form the aforementioned hydrogen bond.

The weak electron-donating effect of the anionic substituent is also well reflected in the calculated frontier orbitals of the model compound **13$_b$b** (Figure 1), because the cationic fragment is joined via a nodal position of the highest occupied molecular orbital (HOMO) to the anionic fragment. This is characteristic of cross-conjugated systems. The HOMO of the NHC tautomer **13$_c$b-I** is a π-orbital with considerable atomic orbital coefficients in the quinazolinonide substituent. As the system is planar in vacuo according to the calculation some small coefficients on N1′ and the carbene carbon atom C2′ have also been

found. The HOMO-1 shows the characteristic σ-lone pair of the NHC, and its lowest unoccupied molecular orbital (LUMO) possesses a considerable atomic orbital coefficient on the carbene carbon atom. The tautomers **13$_c$b-II** and **13$_c$b-III** differ slightly in their frontier orbital geometries and energies (see Fig. S7, Supporting Information). The HOMO of the anionic NHC **13$_{ac}$b** resembles the HOMO of the betaine with respect to its geometry. Interestingly, the HOMO-1 combines the σ-lone pair of the NHC with the σ-framework of the anionic fragment of the quinazolinonide substituent including the free electron pairs of the nitrogen and oxygen atoms.

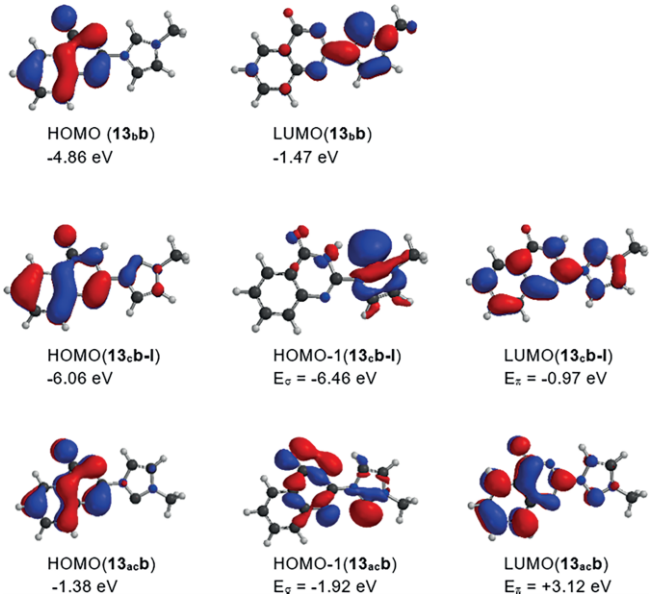


Figure 1. Selected frontier orbitals.

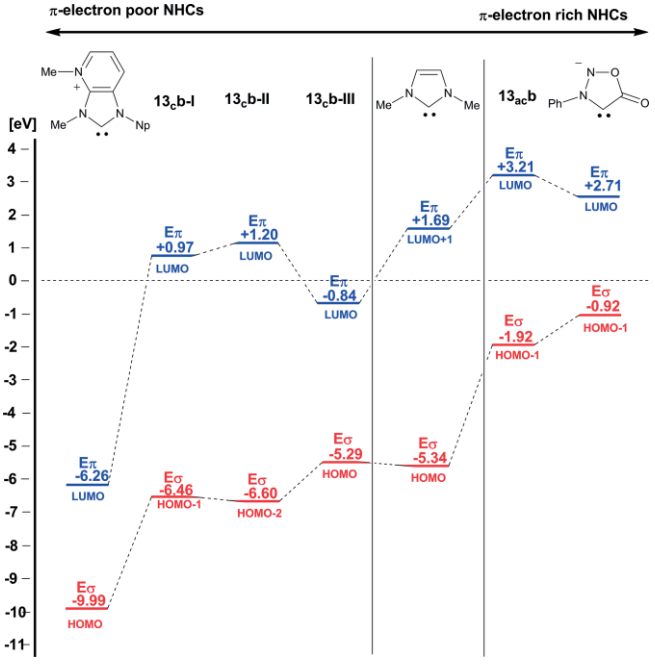
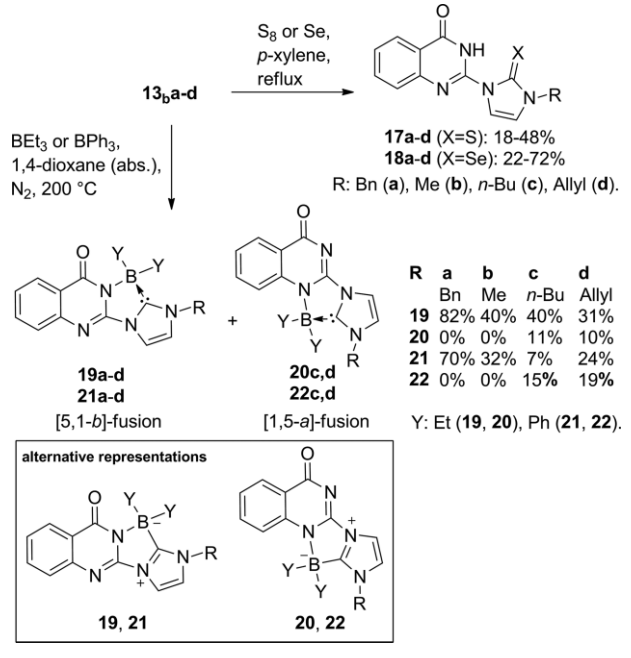


Figure 2. Comparison of relevant frontier orbital energies of the three tautomers **13$_c$b-I–III** and the anionic NHC **13$_{ac}$b** with extremely π-electron poor and π-electron rich NHCs as well as 1,3-dimethylimidazol-2-ylidene as reference compound.

The type of conjugation is also well reflected in the HOMO/LUMO energies. We think that the E$_σ$ energy of **13$_{ac}$b** is lower than those of anionic conjugated N-heterocyclic carbenes such as sydnone carbenes[16] or the extremely π-electron-rich conjugated molsidomine carbene,[17] which we reported earlier, due to the cross-conjugation which induces a π-electronic isolation of the negatively charged substituent with respect to the frontier orbitals. An additional reason might be the better mesomeric stabilization of the anionic charge. A comparison of the HOMO/LUMO energies of the cationic NHC derived from imidazo[4,5-*b*]pyridinium,[37] of the **13** series reported here, of the reference NHC 1,3-dimethylimidazol-2-ylidene, and the conjugated anionic sydnone carbene[16] is displayed in Figure 2. These examples of NHCs cover the range from extremely π-electron poor to extremely π-electron rich.

2.3. Betaine–Carbene Transformations and Trapping Reactions

On treatment of the mesomeric betaines **13$_b$a–d** with sulfur and selenium, respectively, the adducts **17a–d** and **18a–d** of the tautomeric carbenes **13$_c$a–d-I** were obtained in 18–72 % yield (Scheme 5). The ^{77}Se NMR chemical shifts have been first utilized by *Ganter* et al. to determine the π-acceptor strengths of NHCs within the adducts[38] and the method has been applied to numerous NHCs since then.[39] The selenium atoms appear as singlets between 100.57 ppm (**18a**), 104.74 ppm (**18c**) and 120.85 ppm (**18b**) in the ^{77}Se NMR spectra which is indicative of weak π-acceptor capabilities. The values are similar to those of 1,3-dimesitylimidazol-2-ylidene (δ_{Se} = 116 ppm).[35] The corresponding $^1J_{CSe}$ coupling constants were found to be 237 Hz (**18a**), 236 Hz (**18b**), and 237 Hz (**18c**) (Table S4,

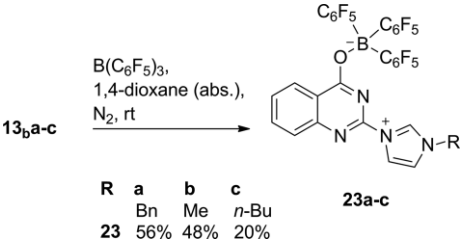


R	a	b	c	d
	Bn	Me	*n*-Bu	Allyl
19	82%	40%	40%	31%
20	0%	0%	11%	10%
21	70%	32%	7%	24%
22	0%	0%	15%	19%

Scheme 5. Trapping reactions of the carbene tautomer with S and Se.

Fig. S4, Supporting Information). These values are indicative of σ-donicities which resemble those of 1,3-di(isopropylphenyl)-4,5-dichloro-imidazol-2-ylidene (239 Hz).[35] We were able to grow single crystals of **17a** and to perform an X-ray crystal structure analysis the molecular drawing of which is shown in the Supporting Information (Fig. S8, Supporting Information). The analysis of this structure revealed an interatomic distance between H3 and the sulfur in position 2′ of 2.205 Å which is significantly smaller than the sum of the van der Waals radii of the corresponding atoms (≈ 3 Å). This indicates the formation of a N3–H···S=C2′ hydrogen bond in the solid state. However, the moderate downfield-shift of the H3 resonances frequencies observed for the case of the sulfur and selenium adducts [δ_H between 13.71 (**18a**) and 14.13 (**17b**) ppm] in comparison to the corresponding value of compound ***14** (13.27 ppm), where such H-bonding is not possible, cannot confirm significant hydrogen bonds in solution. The presence of hydrogen bonds influences δ_{Se} values. We think that their influences are negligible here in view of the very large chemical shift range from 0 to 850 ppm[35] of ^{77}Se resonance frequencies in selenium-NHC adducts.

Triethylborane converted the mesomeric betaines **13$_b$a–d** at 200 °C in anhydrous dioxane into the cyclic borane adducts **19a–d** and **20c,d**, respectively (Scheme 6). The reaction of **13$_b$a,b** with triethylborane led exclusively to the imidazo[2′,1′:3,4]-[1,4,2]diazaborolo[5,1-*b*]quinazolin-12-ides **19a,b**, whereas **13$_b$c,d** gave mixtures of the separable [5,1-*b*] and [1,5-*a*] isomers **19c,d** and **20c,d** in ≈ 3.6:1 and ≈ 3.1:1 ratios under analogous conditions, respectively. Triphenylborane reacted similary to give **21a–d** and **22c,d**. The separable isomers **21c,d** and **22c,d** were formed in ratios of ≈ 1:2.1 and ≈ 1.3:1, respectively. The isomers correspond to the NHC's tautomeric forms **13$_c$a–d-I** and **13$_c$a–d-II** shown in Scheme 4. To the best of our knowledge they are first representatives of new heterocyclic ring systems and are formal trapping adducts of the anionic NHC **13$_{ac}$a–d**. The formation of the borane adducts **19a–d** and **20c,d** was confirmed by the appearance of signals in the range from 1.1 ppm to –0.8 ppm in the 1D ^{11}B NMR spectra, and of **21a–d** and **22c,d** between –1.80 ppm and –2.62 ppm which is the typical range of ^{11}B resonance frequencies of carbene adducts.[28] The resonances of the ^{11}B nuclei and signals of the neighbouring ^{13}C nuclei in the 2′ and 1″ positions were significantly broadened, probably due to the presence of the negative partial charge of the boron atom as indicated by the alternative representations shown in Scheme 5. This made the observation of ^{11}B *J*-couplings impossible. The structure of the compounds **19a–d** and **20c,d**, however, was unambiguously elucidated by analysis of the J_{HN}-couplings in the 2D ^{1}H-^{15}N HMBC NMR experiments which were recorded for samples with natural isotopic abundance of ^{15}N nuclei in [D$_6$]DMSO solution (see 2D ^{1}H-^{15}N HMBC spectra, Supporting Information). The spectra of the isomers **20c,d** showed two cross-peaks corresponding to the vicinal $^3J_{H8\text{-}N1}$ and $^3J_{H1''\text{-}N1}$ couplings which confirm the cyclization via N1 (Figure 3). The nitrogen atoms of the quinazoline moiety of **19a–d** were first assigned by their ^{1}H-^{15}N coupling constants, then the $^3J_{H1''\text{-}N3}$ and $^3J_{H8\text{-}N1}$ couplings confirmed their [1,5-*a*]-fusion.



Scheme 6. Adduct formation via oxygen.

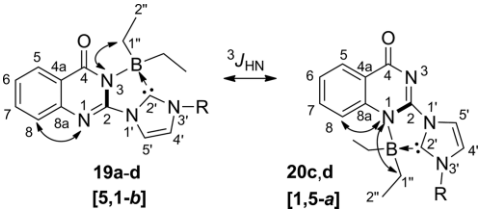


Figure 3. Numbering and diagnostic J_{HN}-couplings.

The NMR-derived structures of the compounds **19a–d** in [D$_6$]DMSO are in agreement with X-ray diffraction data which are obtained for the adduct **19b** (Figure 4). Suitable crystals for an X-ray structure analysis were obtained by slow evaporation of a concentrated solution in ethyl acetate. The compound crystallized in the monoclinic space group $P2_1/c$. The bond lengths between the boron atom and the former carbene carbon atom/quinazoline nitrogen (B1–C3/B1–N3, crystallographic numbering) were determined to be 1.626(3) Å/1.627(2) Å. The bond lengths between the boron atom and the methylene carbon atoms of the ethyl groups were 1.620(3) Å. The four rings benzene, pyrimidine, diazaborole, and imidazole were almost planar. Torsion angles C11–N2–C2–N1 = –3.2(3)°, C10–N1–C2–N3 = 0.1(3)°, C3–N2–C2–N3 = –0.3(2)°, N3–C4–C5–C10 = 1.4(3)° were measured.

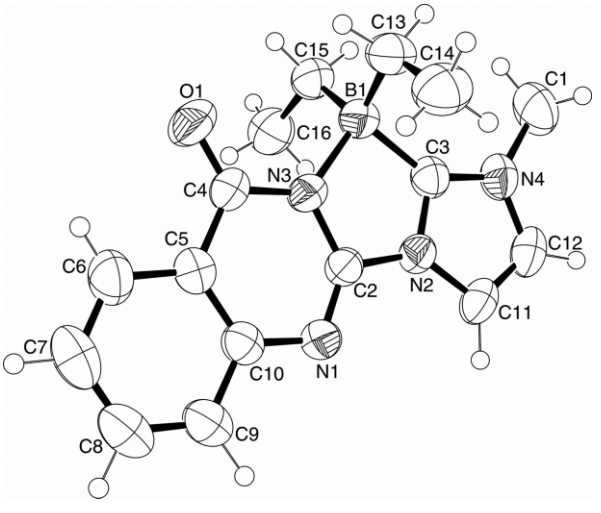


Figure 4. ORTEP diagram of the X-ray structure of compound **19b**.

As recently reviewed,[40] selective ^{15}N-labeling is highly efficient for structure elucidations. As the absence of hydrogen atoms attached to C1″ of **21** and **22** prevented cross-peaks in HMBC measurements, we prepared ***21a,b,d** and ***22d** possess-

ing ^{15}N labels at the N3 positions from ***13a**,**b**,**d** (Figure 5). Thus, the detection of long-range ^{1}H-^{15}N3 interactions in the 2D ^{1}H-^{15}N HMBC spectra and quantitative measurements of the corresponding J_{HN3} (Figures S5 and S6, Supporting Information) as well as of the diagnostic ^{13}C-^{15}N3 *J*-coupling constants was possible (Fig. S1, Supporting Information).

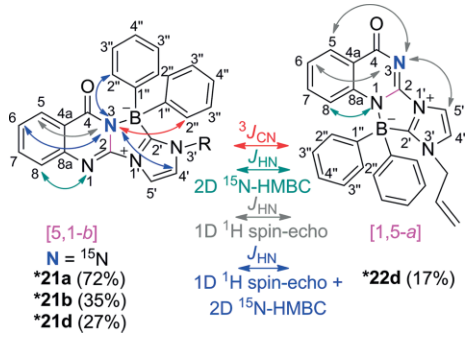


Figure 5. Diagnostic J_{HN} and J_{CN} couplings confirmed structures of the ^{15}N-labeled NHC-borane adducts ***21a**,**b**,**d** and ***22d**. The J_{HN} couplings observed only in 2D ^{1}H-^{15}N-HMBC spectra are shown by green arrows. The blue and gray arrows show $J_{H\text{-}N3}$ > 0.05 Hz, for which quantitative measurements were possible. The measured $^{3}J_{C2''\text{-}N3}$ couplings are shown by a red arrow.

The observed $^{4}J_{H\text{-}N3}$ and $^{3}J_{C\text{-}N3}$ coupling constants (≈ 0.2 and ≈ 0.6 Hz, respectively) with the H2″ and C2″ atoms in *ortho*-position of the phenyl substituents of ***21a**,**b**,**d** unambiguously proved the cyclization via the ^{15}N3-atom (Figure 5, [5,1-*b*]-type of fusion). At the same time, the absence of detectable J_{HN} and J_{CN} couplings between ^{15}N3 and atoms of the phenyl rings implied that the cyclization of ***22d** occurred through the N1 atom ([1,5-*a*]-type of fusion). The small amplitude of $^{1}J_{BN}$ couplings (expected value ≈ 1.5 Hz) and relatively large linewidth of the ^{15}N3 resonances, however, did not allow to measure ^{11}B-^{15}N spin-spin interactions in the compounds ***21a**,**b**, despite of our expectations based on published results.[41] In the parent betaines **13$_b$a**–**d** the ^{15}N1 and ^{15}N3 nuclei resonated in regions around 200 and 215 ppm, respectively. It is interesting to note that the cyclization via the N3 atom (compounds **19a**–**d** and **21a**–**d**) does not influence significantly the ^{15}N1 chemical shifts, but induces an upfield shift of approximately 40 ppm of the ^{15}N3 atoms to ca. 175 ppm (see Fig. S2 and Table S2, Supporting Information). Contrary to that, the cyclization through the N1 atom in compounds **20c**,**d** and **22c**,**d** does not change the chemical shifts of the ^{15}N3 atom, whereas the signals of ^{15}N1 atom shift upfield by ≈ 50 ppm to approximately 150 ppm.

The structures of the isomeric adducts **21a** and **22d** were also proved by X-ray crystallographic analyses (Figure 6). Suitable single crystals of **21a** and **22d** were obtained by slow evaporation of concentrated solutions in acetonitrile. Compound **21a** crystallized with one molecule of acetonitrile in the triclinic space group P1, whereas **22d** crystallized in the monoclinic space group $P2_1/c$. The B–C1 carbene bond lengths (crystallographic numbering) were determined to be 1.643(2) Å (**21a**) and 1.619(3) Å (**22d**), respectively, which is slightly shorter than those of other boron adducts.[28c] The bond lengths between the boron atom and the nitrogen atom N3 and N1 in **21a** and **22d** were found to be 1.618(2) and 1.620(3) Å, respectively. The torsion angles between imidazole and the quinazoline fragment C1–N2–C2–N1 (**21a**) and N1–C2–N3–C4 (**22d**) were determined to be –179.08(14)° and –1.7(3)°. These data confirmed that the quinazoline, diazaborole, and imidazole fragments of **21a** and **22d** are almost planar.

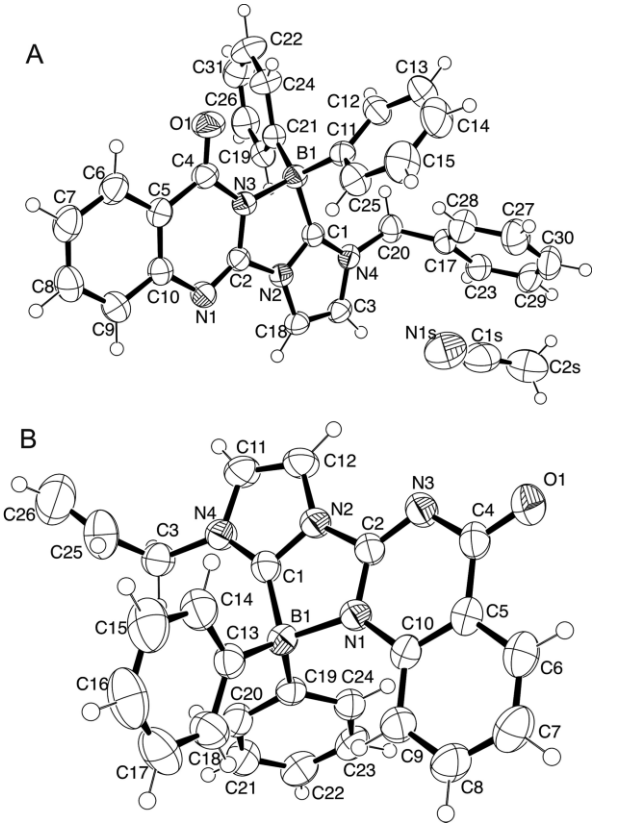


Figure 6. ORTEP diagrams of the X-ray structures of compounds **21a** (a, above) and **22d** (b, below).

Finally, we were also able to form adducts via the oxygen atom of the betaines. Thus, tris(pentafluorophenyl)borane in dioxane at room temperature reacted with **13$_b$a**–**c** to give the borates **23a**–**c** in 56 %, 48 % and 20 % yields, respectively (Scheme 6).

The attachment of the pentafluorophenyl substituent was confirmed by a 2D ^{1}H-^{19}F HOESY spectrum measured for compound **23b**. The spectrum revealed dipolar interactions between the ^{19}F2″ nuclei of the pentafluorophenyl and ^{1}H5 as well as ^{1}H4′, and overlapped ^{1}H6/^{1}H5′ signals of the heterocyclic moiety (Figure 7 and see Figure S135, Supporting Information). The ^{15}N chemical shifts provide additional information about the structure of **23b**. In this case the ^{15}N1 and ^{15}N3 resonances demonstrated only weak downfield shifts relative to the parent betaine **13$_b$b**. They have chemical shifts of ≈ 224 ppm and ≈ 220 ppm, respectively (Table S2 and Fig. S2, Supporting Information). The resonance frequencies of N1′ and N3′ of the imidazole ring also remained essentially unchanged. Thus, the attachment of the boron substituent does not affect the nitrogen atoms, keeping only one possibility of attachment through the oxygen atom.

The NMR analyses were supported by the results of single-crystal X-ray crystallography (Figure 8). Suitable crystals of **23b**

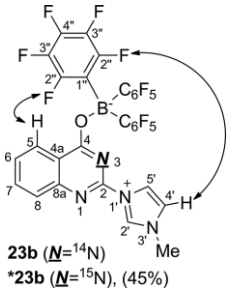


Figure 7. Dipolar ^{1}H, ^{19}F interactions for structure elucidation.

were obtained by slow evaporation from dioxane. The compound **23b** crystallized with 2.5 molecules of 1,4-dioxane in the triclinic space group $P\bar{1}$. The boron atom is surrounded by three carbon atoms of three pentafluorophenyl rings and one oxygen atom of the ligand. The B–C bonds were found to be 1.643(3), 1.644(3), and 1.649(3) Å, which correspond to the values of the bond lengths in the literature-known tris(perfluorophenyl)-borate of 2-(3-alkyl-1*H*-imidazolium-1-yl)phenolates.[42] The B–O bond has a length of 1.522(3) Å. This is in analogy to the B–O distance of $B(C_6F_5)_3$ adducts of formate (1.532 Å),[43] or 2-(pyridin-2-yl)phenol (1.520 Å).[44] The polyhedron BC_3O is tetrahedral with bond angles C–B1–O1 and C–B1–C in the range of 103.1(2)–112.0(2)° and 106.3(2)–114.6(2)°, respectively.

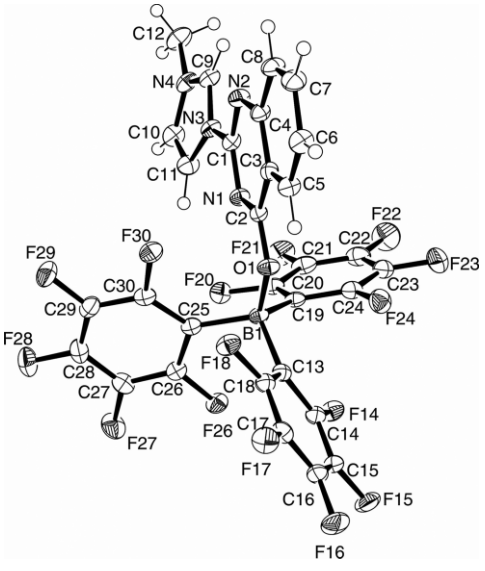


Figure 8. ORTEP diagram of the X-ray structure of borane adduct **23b**.

Conclusions

The mesomeric betaines 2-(1-alkyl-1*H*-imidazolium-3-yl)quinazolin-4-olates are cross-conjugated and *crypto*-N-heterocyclic carbenes. The latter can be formulated as three different tautomers or as anionic N-heterocyclic carbene after deprotonation. Imidazole-2-thiones and imidazole-2-selenones were obtained on reaction of sulfur and selenium, respectively, with the betaines, which behave as N-heterocyclic carbenes under these conditions. The usage of triethylborane and triphenylborane led to new cyclic borane adducts, imidazo[2′,1′:3,4][1,4,2]diazaborolo-[5,1-*b*]quinazoline-12-ides and their [1,5-*a*]-isomers. These are formal trapping products of the anionic NHC and represent the translation of different tautomers into new structures of cyclic borane adducts. Structures were confirmed by analysis of ^{1}H-^{15}N *J*-couplings and ^{15}N chemical shifts at natural isotopic abundance and upon selective ^{15}N-labeling of the N3 position in the 4-oxoquinazolinide fragment. The ^{15}N chemical shift data and through-space dipolar correlations observed in 2D ^{1}H-^{19}F HOESY spectra turned out to be useful for the identification of noncyclic adducts containing pentafluorophenyl groups. The σ-donating and π-accepting properties of the N-heterocyclic carbenes were estimated by analysis of $^{1}J_{CSe}$ and $^{1}J_{HC}$ coupling constants as well ^{77}Se resonance frequencies. In accordance with their classification as cross-conjugated systems and in contrast to conjugated systems, the anionic substituent takes only a weak influence on the characteristics of the corresponding NHCs. These results supplement on the one hand our knowledge about the intersection of the two substance classes of N-heterocyclic carbenes and mesomeric betaines which are *crypto*-NHCs depending on their type of conjugation, and on the other hand our knowledge about boron adducts of NHCs.[45]

Experimental Section

All reactions were carried out under an atmosphere of nitrogen in flame or oven-dried glassware. All chemicals were purchased and used without further purification unless otherwise mentioned. Anhydrous solvents were dried according to standard procedures before usage. Melting points are uncorrected and were determined in an apparatus according to Dr. Tottoli (Büchi). The ATR-IR spectra were obtained on a Bruker Alpha in the range of 400 to 4000 cm^{-1}. ^{1}H, ^{11}B, ^{13}C, ^{15}N, ^{19}F and ^{77}Se NMR spectra were measured in [D_6]DMSO solution using Bruker AVANCE-II-400 or Bruker NEO 600 spectrometers equipped with room temperature broadband probes, or using a Bruker AVANCE-700 spectrometer equipped with a triple-resonance (^{1}H, ^{13}C, ^{15}N) room-temperature probe. ^{1}H chemical shifts were referenced to the DMSO signal which appeared at 2.50 ppm. Chemical shifts of ^{11}B, ^{13}C, ^{15}N, ^{19}F, and ^{77}Se nuclei were referenced indirectly relative to boron trifluoride etherate, Me_4Si, liquid ammonium, CCl_3F and Me_2Se, respectively. Multiplicities are described by using the following abbreviations: s = singlet, d = doublet, t = triplet, q = quartet, and m = multiplet. The assignment of all ^{1}H and ^{13}C resonances was achieved using gradient enhanced versions of 2D NMR ^{1}H-^{13}C HSQC, and ^{1}H-^{13}C HMBC experiments. The assignment of ^{15}N atoms (labeled or at natural abundance) was based on 2D ^{1}H-^{15}N HMBC experiments. The measurements of $J_{H\text{-}C}$, $J_{H\text{-}N}$, $J_{C\text{-}N}$ and $J_{C\text{-}Se}$ coupling constants are described in the Supporting Information. The mass spectra (ESIMS) were measured with a Varian 320 MS Triple Quad GC/MS/MS (EIMS) or with an Agilent LCMSD series HP 1100 with APIES at fragmentor voltages as indicated. Samples were sprayed from MeOH at 4000 V capillary voltage and fragmentor voltages of 30 V unless otherwise noted. The HRMS spectra were obtained with a Bruker Impact II, a Bruker Daltonik Tesla–Fourier transform-ion cyclotron resonance mass spectrometer, or with a Waters Micromass LCT with the direct inlet. Chromatography: The reactions were traced by thin layer chromatography with silica gel 60 (F254, company MERCK KGAA). For the detection of substances, quenching was used at either 254 nm or 366 nm with a mercury lamp. The preparative column chroma-

tography was conducted through silica gel 60 (230 400 mesh) of the company MERCK KGAA. Yields are not optimized.

Crystal Structure Determinations

The X-ray diffraction data of the compounds **17a**, **19b**, **21a** and **22d** were collected on a Xcalibur S diffractometer with Mo-K_α radiation (λ = 0.71073 Å, graphite monochromator, $\omega/2\theta$-scanning technique). Unit cell parameters were refined using all collected spots after the integration process. The structures were solved by direct methods that were implemented in the SHELXS-97 program.[46] The refinements were carried out through full-matrix anisotropic least-squares methods on F^2 for all reflections of the non-H atoms using the SHELXL-97 program.[47] The single-crystal X-ray diffraction studies of compound **23b** were carried out on a Bruker SMART APEX II diffractometer equipped with a CCD detector (Mo-K_α, λ = 0.71073 Å, graphite monochromator). Semiempirical absorption correction was applied.[48] The structures were solved by direct methods and refined by the full-matrix least-squares with anisotropic displacement parameters using the SHELX-2014 program package.[49] The hydrogen atoms of the ligands were positioned geometrically and refined using the riding model.

CCDC 1938079 (for **17a**), 1938188 (for **19b**), 1938147 (for **21a**), 1938162 (for **22d**), and 1917533 (for **23b**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

17a: Colorless crystals, $C_{18}H_{14}N_4OS$, M = 334.39, crystal size 0.45 × 0.35 × 0.25 mm, monoclinic system, space group *P*2(1)/*c*, *a* = 7.3155(10) Å, *b* = 23.103(3) Å, *c* = 9.8773(15) Å, α = 90.00°, β = 110.912(13)°, γ = 90°, *V* = 1559.4(4) Å^3, *Z* = 4, ρ_{calc} = 1.424 g cm^{-3}, μ = 0.220 cm^{-1}, 8796 measured reflections, 1688 reflections with $I > 2.0\sigma(I)$, R_{int} = 0.0398, *GooF* = 1.007, R_1 [$I > 2\sigma(I)$] = 0.0395, wR_2 [$I > 2\sigma(I)$] = 0.0614, R_1 (all data) = 0.0989, wR_2 (all data) = 0.0646, $T_{min/max}$ = 0.8364/1.1692.

19b: Colorless crystals, $C_{16}H_{19}BN_4O$, M = 294.16, crystal size 0.48 × 0.36 × 0.24 mm, monoclinic system, space group *P*2(1)/*c*, *a* = 7.3715(5) Å, *b* = 12.8142(8) Å, *c* = 16.7820(14) Å, α = 90°, β = 92.686(6)°, γ = 90°, *V* = 1583.5(2) Å^3, *Z* = 4, ρ_{calc} = 1.234 g cm^{-3}, μ = 0.079 cm^{-1}, 9474 measured reflections, 2437 reflections with $I > 2.0\sigma(I)$, R_{int} = 0.0336, *GooF* = 1.004, R_1 [$I > 2\sigma(I)$] = 0.0573, wR_2 [$I > 2\sigma(I)$] = 0.1518, R_1 (all data) = 0.1047, wR_2 (all data) = 0.2039, $T_{min/max}$ = 0.7537/1.0000.

21a: Colorless crystals, $C_{32}H_{26}BN_5O$, M = 507.39, crystal size 0.49 × 0.38 × 0.26 mm, triclinic system, space group $P\bar{1}$, *a* = 11.0751(7) Å, *b* = 11.4438(8) Å, *c* = 11.7557(8) Å, α = 69.231(6)°, β = 72.687(6)°, γ = 83.101(5)°, *V* = 1329.82(15) Å^3, *Z* = 2, ρ_{calc} = 1.267 g cm^{-3}, μ = 0.078 cm^{-1}, 10466 measured reflections, 4344 reflections with $I > 2.0\sigma(I)$, R_{int} = 0.0265, *GooF* = 1.008, R_1 [$I > 2\sigma(I)$] = 0.0540, wR_2 [$I > 2\sigma(I)$] = 0.1472, R_1 (all data) = 0.0894, wR_2 (all data) = 0.1869, $T_{min/max}$ = 0.7927/1.0000.

22d: Colorless crystals, $C_{26}H_{21}BN_4O$, M = 416.28, crystal size 0.41 × 0.33 × 0.20 mm, monoclinic system, space group *P*2(1)/*c*, *a* = 14.3210(16) Å, *b* = 9.3202(7) Å, *c* = 16.4475(15) Å, α = 90.00°, β = 98.942(10)°, γ = 90°, *V* = 2168.6(4) Å^3, *Z* = 4, ρ_{calc} = 1.275 g cm^{-3}, μ = 0.079 cm^{-1}, 14741 measured reflections, 2802 reflections with $I > 2.0\sigma(I)$, R_{int} = 0.0526, *GooF* = 1.000, R_1 [$I > 2\sigma(I)$] = 0.0593, wR_2 [$I > 2\sigma(I)$] = 0.1291, R_1 (all data) = 0.1446, wR_2 (all data) = 0.1797, $T_{min/max}$ = 0.8001/1.0000.

23b: Colorless crystals, $C_{40}H_{30}BF_{15}N_4O_6$, M = 958.49, colorless, parallelepiped, crystal size 0.30 × 0.20 × 0.10, triclinic system, space group $P\bar{1}$, *a* = 11.0423(3) Å, *b* = 12.3276(3) Å, *c* = 16.2662(4) Å, α = 73.3220(10)°, β = 71.0790(10)°, γ = 78.0130(10)°, *V* = 1990.36(9) Å^3, *Z* = 2, ρ_{calc} = 1.599 g cm^{-3}, μ = 0.154 cm^{-1}, 18405 measured reflections, 6664 reflections with $I > 2.0\sigma(I)$, R_{int} = 0.0226, *GooF* = 1.030, R_1 [$I > 2\sigma(I)$] = 0.0508, wR_2 [$I > 2\sigma(I)$] = 0.1357, R_1 (all data) = 0.0616, wR_2 (all data) = 0.1434, $T_{min/max}$ = 0.661/0.745.

Calculations

All density-functional theory (DFT)-calculations were carried out applying the current Spartan Software (*Spartan'18*, Wavefunction, Inc., Irvine, CA. Available from: http://www.wavefun.com) running on an Intel® Core™ i7–6950X decacore system equipped with 64 GB RAM main memory and sufficient solid-state disc space. MM2 optimized structures were used as starting geometries. Complete geometry calculations were performed with the PBE0 density functional and the implemented 6-31G* basis set in order to allow for comparison with previous results. All final structures were proven to be true minima by the absence of imaginary frequencies.

Synthesis

Compound **14** was prepared according to previously published protocols.[50] The synthesis of ***14** is presented in the Supporting Information.

2-(1-Benzyl-1*H*-imidazolium-3-yl)quinazolin-4-olate (13$_b$a): A 150 mL portion of the anion-exchange resin Amberlite IRA-400 was filled into a column (height: 16 cm, diameter: 3 cm) and washed with 2 L of water. Then 100 mL of a 5 % hydrochloric acid solution was added and remained in the column for 2 h. The hydrochloric acid was then rinsed out with water until pH 7 was reached. 100 mL of a 5 % aqueous solution of sodium hydroxide was added and remained in the column for 2 h. Then the base was rinsed out with water until pH = 7 was reached. Then, samples of salts **16** (0.677 g, 2.0 mmol) in 60 mL of water were added on the resin. After that, the resulting betaine was extracted with ethyl acetate and solvent was evaporated in vacuo. Yield 0.508 g, 84 %, colorless solid, m.p. > 252 °C (dec.). ^{1}H NMR (600 MHz, [D$_6$]DMSO): δ = 5.51 (s, 2H, H6′), 7.25 (ddd, ^1J = 7.9 Hz, ^2J = 6.9 Hz, ^3J = 1.1 Hz, 1H, H6), 7.38–7.45 (m, 3H, H9′,H10′), 7.46 (ddd, ^1J = 8.2 Hz, ^2J = 1.1 Hz, ^3J = 0.5 Hz, 1H, H8), 7.52–7.54 (m, 2H, H8′), 7.56 (ddd, ^1J = 8.3 Hz, ^2J = 6.9 Hz, ^3J = 1.5 Hz, 1H, H7), 7.86 (t, ^1J = 1.86 Hz, 1H, H4′), 8.00 (ddd, ^1J = 7.9 Hz, ^2J = 1.5 Hz, ^3J = 0.4 Hz, 1H, H5), 8.32 (t, ^1J = 1.83 Hz, 1H, H5′), 10.13 (d, ^1J = 1.6, 1H, H2′) ppm. ^{13}C NMR (151 MHz, [D$_6$]DMSO): δ = 52.29 (C6′), 119.32 (C5′), 122.60 (C4′), 122.85 (C4a), 123.53 (C6), 125.39 (C8), 126.25 (C5), 128.48 (C8′), 128.80 (C10′), 129.03 (C9′), 131.69 (C7), 134.81 (C7′), 134.9 (C2′), 150.60 (C8a), 151.96 (C2), 171.33 (C4) ppm. IR (ATR): $\tilde{\nu}$ = 3024, 1580, 1530, 1472, 1450, 1367, 1077, 1029, 926, 768, 744, 695, 631 cm^{-1}. HRMS (ESI) *m/z* calcd. for $C_{18}H_{14}N_4ONa$ [M + Na]$^+$ 325.1065, found 325.1058; elemental analysis calcd. (%) for $C_{18}H_{14}N_4O$: C 71.51, H 4.67, N 18.53; found C 71.41, H 4.55, N 18.78.

[3-^{15}N]-2-(1-Benzyl-1*H*-imidazolium-3-yl)quinazolin-4-olate (*13$_b$a): Synthesized as described for **13a**. Yield 0.181 g, 60 %, colorless solid, m.p. > 252 °C (dec.). ^{1}H NMR (600 MHz, [D$_6$]DMSO): δ = 5.51 (s, 2H, H6′), 7.25 (ddd, ^1J = 7.9 Hz, ^2J = 6.9 Hz, ^3J = 1.1 Hz, 1H, H6), 7.38–7.45 (m, 3H, H9′,H10′), 7.46 (ddd, ^1J = 8.2 Hz, ^2J = 1.1 Hz, ^3J = 0.5 Hz, 1H, H8), 7.52–7.54 (m, 2H, H8′), 7.56 (ddd, ^1J = 8.3 Hz, ^2J = 6.9 Hz, ^3J = 1.5 Hz, 1H, H7), 7.86 (t, ^1J = 1.86 Hz, 1H, H4′), 8.00 (ddd, ^1J = 7.9 Hz, ^2J = 1.5 Hz, ^3J = 0.4 Hz, 1H, H5), 8.32 (t, ^1J = 1.7 Hz, 1H, H5′), 10.13 (s, 1H, H2′) ppm. ^{13}C NMR (151 MHz, [D$_6$]DMSO): δ = 52.27 (C6′), 119.30 (d, ^3J = 1.5 Hz, C5′), 122.58 (C4′), 122.86 (d, ^2J = 2.4 Hz, C4a), 123.49 (C6), 125.37 (C8), 126.23 (br. s, C5), 128.48 (C8′), 128.79 (C10′), 129.03 (C9′), 131.66 (C7), 134.82 (C7′), 134.90 (d, ^3J = 2.5 Hz, C2′), 150.59 (C8a), 151.95 (d, ^1J = 4.6 Hz, C2), 171.25 (d, ^1J = 4.3 Hz, C4) ppm. IR (ATR): $\tilde{\nu}$ = 3024, 1580, 1530, 1472, 1450,

1367, 1077, 1029, 926, 768, 744, 695, 631 cm^{-1}. HRMS (ESI) *m/z* calcd. for $C_{18}H_{14}{}^{15}NN_3ONa$ $[M + Na]^+$ 326.1036, found 326.1034.

General Procedure for the Synthesis of the Betaines 13_bb, 13_bd: Under an inert atmosphere a mixture of 2-chloroquinazolin-4(3*H*)-one (180 mg, 1.0 mmol) and 2 equiv. excess of corresponding imidazoles (2.0 mmol) was stirred at 100–105 °C for 2 h without solvent. After stirring mixture was cooled to r.t., added $CHCl_3$ (**13_bb**) or dioxane (**13_bd**), then the resulting precipitates were filtered off, washed with a small amount of $CHCl_3$ (**13_bb**) or dioxane (**13_bd**) and dried.

2-(1-Methyl-1*H*-imidazolium-3-yl)quinazolin-4-olate (13_bb): 1-Methylimidazole (161 μL, 2.0 mmol) was used. Recrystallization from *i*PrOH gave **13_bb**. Yield 0.150 g, 67 % colorless solid, m.p. > 198 °C (dec.). ^1H NMR (600 MHz, $[D_6]$DMSO): δ = 3.94 (s, 3H, H6′), 7.26 (t, ^1J = 7.4 Hz, 1H, H6), 7.46 (d, ^1J = 8.0 Hz, 1H, H8), 7.57 (t, ^1J = 7.4 Hz, 1H, H7), 7.78 (s, 1H, H4′), 8.01 (dd, ^1J = 7.9 Hz, ^2J = 1.0 Hz, 1H, H5), 8.29 (t, ^1J = 1.6 Hz, 1H, H5′), 9.88 (s, 1H, H2′) ppm. ^{13}C NMR (151 MHz, $[D_6]$DMSO): δ = 36.10 (C6′), 118.60 (C5′), 122.68 (C4a), 123.60 (C6), 123.88 (C4′), 125.41 (C8), 126.22 (C5), 131.79 (C7), 135.46 (C2′), 150.55 (C8a), 151.72 (C2), 171.13 (C4) ppm. IR (ATR): $\tilde{\nu}$ = 3390, 3086, 1592, 1576, 1541, 1471, 1349, 1268, 1112, 1077, 926, 846, 775, 698, 617 cm^{-1}. HRMS (ESI) *m/z* calcd. for $C_{12}H_{10}N_4ONa$ $[M + Na]^+$ 249.0752, found 249.0746.

[3-^{15}N]-2-(1-Methyl-1*H*-imidazolium-3-yl)quinazolin-4-olate (*13_bb): Synthesized as described for **13_bb**. Yield 0.158 g, 70 %, colorless solid, m.p. > 198 °C (dec.). ^1H NMR (600 MHz, $[D_6]$DMSO): δ = 3.96 (s, 3H, H6′), 7.34 (t, ^1J = 7.1 Hz, 1H, H6), 7.53 (d, ^1J = 8.1 Hz, 1H, H8), 7.66 (t, ^1J = 7.4 Hz, 1H, H7), 7.83 (s, 1H, H4′), 8.05 (dd, ^1J = 7.9 Hz, ^2J = 1.0 Hz, 1H, H5), 8.31 (t, ^1J = 1.6 Hz, 1H, H5′), 9.92 (s, 1H, H2′) ppm. ^{13}C NMR (151 MHz, $[D_6]$DMSO): δ = 36.22 (C6′), 118.81 (C5′), 121.89 (br. s, C4a), 124.05 (C6), 124.50 (C4′), 125.71 (C8), 126.15 (C5), 132.62 (C7), 135.73 (C2′), 150.01 (C8a), 150.06 (d, ^1J = 6.9 Hz, C2), 169.93 (d, ^1J = 5.7 Hz, C4) ppm. IR (ATR): $\tilde{\nu}$ = 3390, 3086, 1592, 1576, 1541, 1471, 1349, 1268, 1112, 1077, 926, 846, 775, 698, 617 cm^{-1}. HRMS (ESI) *m/z* calcd. for $C_{12}H_{10}{}^{15}NN_3ONa$ $[M + Na]^+$ 250.0723, found 250.0722.

2-(1-Butyl-1*H*-imidazolium-3-yl)quinazolin-4-olate (13_bc): Under an inert atmosphere a mixture of 2-chloroquinazolin-4(3*H*)-one (180 mg, 1.0 mmol) and 2 equiv. excess of 1-butylimidazole (262 μL, 2.0 mmol) was stirred at 100–105 °C for 2 h without solvent. After stirring mixture was cooled to r.t., the resulting mixture was purified by column chromatography (silica gel, elution gradient ethyl acetate → ethyl acetate/MeOH, 5:1). Yield 0.145 g, 54 %, colorless solid, m.p. 174 °C. ^1H NMR (600 MHz, $[D_6]$DMSO): δ = 0.92 (t, ^1J = 7.4 Hz, 3H, H9′), 1.33–1.25 (m, 2H, H8′), 1.88–1.82 (m, 2H, H7′), 4.28 (t, ^1J = 7.2 Hz, 2H, H6′), 7.28–7.25 (m, 1H, H6), 7.47 (d, ^1J = 7.7 Hz, 1H, H8), 7.58 (ddd, ^1J = 8.4 Hz, ^2J = 7.0 Hz, ^3J = 1.6 Hz, 1H, H7), 7.90 (t, ^1J = 1.8 Hz, 1H, H4′), 8.01 (dd, ^1J = 7.9 Hz, ^2J = 1.2 Hz, 1H, H5), 8.33 (t, ^1J = 1.8 Hz, 1H, H5′), 9.97 (s, 1H, H2′) ppm. ^{13}C NMR (151 MHz, $[D_6]$DMSO): δ = 13.29 (C9′), 18.83 (C8′), 31.27 (C7′), 48.94 (C6′), 118.96 (C5′), 122.61 (C4′), 122.68 (C4a), 123.61 (C6), 125.41 (C8), 126.22 (C5), 131.80 (C7), 134.87 (C2′), 150.53 (C8a), 151.71 (C2), 171.13 (C4) ppm. IR (ATR): $\tilde{\nu}$ = 3211, 3079, 3015, 2955, 1531, 1501, 1454, 1378, 1337, 1276, 1153, 1083, 1028, 921, 769, 690, 636 cm^{-1}. HRMS (ESI) *m/z* calcd. for $C_{15}H_{16}N_4ONa$ $[M + Na]^+$ 291.1222, found 291.1220.

2-(1-Allyl-1*H*-imidazolium-3-yl)quinazolin-4-olate (13_bd): 1-Allylimidazole (216 μL, 2.0 mmol) was used. Recrystallization from *i*PrOH gave **13_bd**. Yield 0.190 g, 75 %, colorless solid, m.p. > 260 °C (dec.). ^1H NMR (600 MHz, $[D_6]$DMSO): δ = 4.94 (d, ^1J = 6.0 Hz, 2H, H6′), 5.35–5.39 (m, 2H, H8′), 6.13 (ddt, ^1J = 16.4 Hz, ^2J = 10.3 Hz, ^3J = 6.1 Hz, 1H, H7′), 7.25 (ddd, ^1J = 8.0 Hz, ^2J = 7.0 Hz, ^3J = 1.2 Hz, 1H, H6), 7.47 (dd, ^1J = 8.2 Hz, ^2J = 0.6 Hz, 1H, H8), 7.57 (ddd, ^1J = 8.4 Hz, ^2J = 7.0 Hz, ^3J = 1.6 Hz, 1H, H7), 7.80 (t, ^1J = 1.9 Hz, 1H, H4′), 8.00 (dd, ^1J = 7.9 Hz, ^2J = 1.2 Hz, 1H, H5), 8.34 (t, ^1J = 1.8 Hz, H5′), 9.94 (t, ^1J = 1.6 Hz, 1H, H2′) ppm. ^{13}C NMR (151 MHz, $[D_6]$DMSO): δ = 51.20 (C6′), 119.03 (C5′), 120.36 (C8′), 122.63 (C4′), 122.81 (C4a), 123.53 (C6), 125.38 (C8), 126.24 (C5), 131.70 (C7), 131.84 (C7′), 134.94 (C2′), 150.58 (C8a), 151.90 (C2), 171.26 (C4) ppm. IR (ATR): $\tilde{\nu}$ = 3048, 2953, 2656, 1687, 1626, 1579, 1506, 1455, 1358, 1308, 1258, 1078, 918, 790, 766, 700, 608 cm^{-1}. HRMS (ESI) *m/z* calcd. for $C_{14}H_{12}N_4ONa$ $[M + Na]^+$ 275.0909, found 275.0909; elemental analysis calcd. (%) for $C_{14}H_{12}N_4O$: C 66.65, H 4.79, N 22.21; found C 66.55, H 4.72, N 22.43.

[3-^{15}N]-2-(1-Allyl-1*H*-imidazolium-3-yl)quinazolin-4-olate (*13_bd): Synthesized as described for **13_bd**. Yield 0.184 g, 73 %, colorless solid, m.p. > 260 °C (dec.). ^1H NMR (600 MHz, $[D_6]$DMSO): δ = 4.94 (d, ^1J = 6.0 Hz, 2H, H6′), 5.35–5.39 (m, 2H, H8′), 6.13 (ddt, ^1J = 16.4 Hz, ^2J = 10.3 Hz, ^3J = 6.1 Hz, 1H, H7′), 7.25 (ddd, ^1J = 8.0 Hz, ^2J = 7.0 Hz, ^3J = 1.2 Hz, 1H, H6), 7.47 (dd, ^1J = 8.2 Hz, ^2J = 0.6 Hz, 1H, H8), 7.57 (ddd, ^1J = 8.4 Hz, ^2J = 7.0 Hz, ^3J = 1.6 Hz, 1H, H7), 7.80 (t, ^1J = 1.9 Hz, 1H, H4′), 8.00 (dd, ^1J = 7.9 Hz, ^2J = 1.2 Hz, 1H, H5), 8.34 (t, ^1J = 1.8 Hz, H5′), 9.94 (t, ^1J = 1.6 Hz, 1H, H2′) ppm. ^{13}C NMR (150 MHz, $[D_6]$DMSO): δ = 51.19 (C6′), 119.01 (br. s, C5′), 120.34 (C8′), 122.63 (C4′), 122.84 (d, ^2J = 1.6 Hz, C4a), 123.48 (C6), 125.37 (C8), 126.23 (C5), 131.67 (C7), 131.86 (C7′), 134.92 (br. s, C2′), 150.61 (C8a), 151.95 (d, ^1J = 4.4 Hz, C2), 171.28 (d, ^1J = 4.0 Hz, C4) ppm. IR (ATR): $\tilde{\nu}$ = 3048, 2953, 2656, 1687, 1626, 1579, 1506, 1455, 1358, 1308, 1258, 1078, 918, 790, 766, 700, 608 cm^{-1}. HRMS (ESI) *m/z* calcd. for $C_{14}H_{12}{}^{15}NN_3ONa$ $[M + Na]^+$ 276.0879, found 276.0868.

1-Benzyl-3-(4-hydroxyquinazolin-2-yl)-1*H*-imidazol-3-ium Chloride (16): A solution of 2-chloroquinazolin-4(3*H*)-one (360 mg, 2.0 mmol) and 2 equiv. excess of 1-benzyl-1*H*-imidazole (632 mg, 4.0 mmol) in 10 mL of 1,2-DCB was stirred at 100–105 °C for 2 h. After stirring the precipitates were filtered off, washed with a small amount of $CHCl_3$ and dried. Yield 0.550 g, 81 %, colorless solid, m.p. > 227 °C (dec.). ^1H NMR (600 MHz, $[D_6]$DMSO): δ = 5.64 (s, 2H, H6′), 7.44–7.40 (m, 1H, H10′), 7.46 (t, ^1J = 7.3 Hz, 2H, H9′), 7.57 (d, ^1J = 7.3 Hz, 2H, H8′), 7.64 (t, ^1J = 7.6 Hz, 1H, H6), 7.79 (d, ^1J = 8.2 Hz, 1H, H8), 7.95 (t, ^1J = 7.7 Hz, 1H, H7), 8.09 (s, 1H, H4′), 8.21 (d, ^1J = 7.6 Hz, 1H, H5), 8.45 (s, 1H, H5′), 10.31 (s, 1H, H2′) ppm. ^{13}C NMR (151 MHz, $[D_6]$DMSO): δ = 52.59 (C6′), 119.33 (C4a), 120.34 (C5′), 123.23 (C4′), 125.96 (C5), 126.71 (C8), 127.61 (C6), 128.68 (C8′), 128.96 (C10′), 129.02 (C9′). 134.32 (C7′), 135.44 (C7), 136.38 (C2′), 144.00 (C2), 147.84 (C8a), 165.04 (C4) ppm. ^{15}N NMR (61 MHz, $[D_6]$DMSO): δ = 190.29 (N3′) ppm. IR (ATR): $\tilde{\nu}$ = 3186, 3054, 2930, 2824, 2675, 1694, 1629, 1578, 1456, 1359, 1311, 1265, 1107, 1078, 1026, 894, 794, 764, 701, 628, 462 cm^{-1}. HRMS (ESI) *m/z* calcd. for $C_{18}H_{14}N_4ONa$ $[M + Na]^+$ 325.1065, found 325.1050. Elementary analysis: calcd. for $C_{18}H_{15}ClN_4O$, %: C 63.81; H 4.46; N 16.54, Cl 10.46; found, %: 63.65; H 4.42; N 16.44, Cl 10.14.

[3-^{15}N]-1-Benzyl-3-(4-hydroxyquinazolin-2-yl)-1*H*-imidazol-3-ium Chloride (*16): Synthesized as described for **16**. Yield 0.366 g, 54 %, colorless solid, m.p. > 227 °C (dec.). ^1H NMR (600 MHz, $[D_6]$DMSO): δ = 5.63 (s, 2H, H6′), 7.49–7.39 (m, 3H, H10′, 59′), 7.57 (d, ^1J = 7.1 Hz, 2H, H8′), 7.65 (t, ^1J = 7.2 Hz, 1H, H6), 7.79 (d, ^1J = 8.2 Hz, 1H, H8), 7.95 (t, ^1J = 8.4 Hz, 1H, H7), 8.08 (s, 1H, H4′), 8.21 (dd, ^1J = 8.0 Hz, ^2J = 0.9 Hz, 1H, H5), 8.44 (s, 1H, H5′), 10.29 (s, 1H, H2′) ppm. ^{13}C NMR (600 MHz, $[D_6]$DMSO): δ = 52.61 (C6′), 119.37 (br. s, C4a), 120.35 (C5′), 123.23 (C4′), 125.97 (C5), 126.74 (br. s, C8), 127.62 (C6), 128.68 (C8′), 128.98 (C10′), 129.04 (C9′). 134.32 (C7′), 135.45 (C7), 136.37 (C2′), 144.03 (br. s, C2), 147.89 (br. s, C8a), 165.05 (br. s, C4) ppm. IR (ATR): $\tilde{\nu}$ = 3186, 3054, 2930, 2824, 2675, 1694,

1629, 1578, 1456, 1359, 1311, 1265, 1107, 1078, 1026, 894, 794, 764, 701, 628, 462 cm^{-1}. HRMS (ESI) *m/z* calcd. for $C_{18}H_{14}{}^{15}NN_3ONa$ $[M + Na]^+$ 326.1036, found 326.1033.

General Procedure for the Formation of Thiones 17a–d and Selenones 18a–d: Under an inert atmosphere a solution of 0.5 mmol betaine and 3 equiv. excess of sulfur (48 mg, 1.5 mmol) or selenium (118.5 mg, 1.5 mmol) in 10 mL of dry *p*-xylene was refluxed for 48 h. After evaporation, the resulting precipitate was purified by column chromatography (silica gel, elution gradient petroleum ether → petroleum ether/ethyl acetate, 2:1).

2-(3-Benzyl-2-thioxo-2,3-dihydro-1*H*-imidazol-1-yl)quinazolin-4(3*H*)-one (17a): A sample of the betaine **13a** (151 mg, 0.5 mmol) was used. The thione **19a** was obtained as solid. Yield 0.50 g, 30 %, colorless solid, m.p. > 247 °C (dec.). ^{1}H NMR (600 MHz, [D$_6$]DMSO): δ = 5.31 (s, 2H, C6′), 7.35–7.31 (m, 1H, H10′), 7.40–7.36 (m, 4H, H8′, H9′), 7.51 (d, ^1J = 2.7 Hz, 1H, H4′), 7.57–7.52 (m, 1H, H6), 7.68 (d, ^1J = 8.1 Hz, 1H, H8), 7.86 (ddd, ^1J = 8.4 Hz, ^2J = 7.3 Hz, ^3J = 1.5 Hz, 1H, H7), 7.96 (d, ^1J = 2.7 Hz, 1H, H5′), 8.15 (dd, ^1J = 7.9 Hz, ^2J = 1.2 Hz, 1H, H5), 13.98 (s, 1H, H3) ppm. ^{13}C NMR (151 MHz, [D$_6$]DMSO): δ = 49.61 (C6′), 115.64 (C5′), 119.88 (C4′), 120.72 (C4a), 126.21 (C5), 126.62 (C6),126.87 (C8), 127.82 (C9′, C10′), 128.56 (C8′), 135.01 (C7), 135.54 (C7′), 143.61 (C2), 147.47 (C8a), 160.36 (C4), 161.35 (C2′) ppm. IR (ATR): $\tilde{\nu}$ = 3188, 3153, 3112, 3030, 2872, 2825, 1678, 1619, 1564, 1514, 1447, 1393, 1243, 1150, 797, 747, 717, 699, 659, 633, 530, 466 cm^{-1}. HRMS (ESI) *m/z* calcd. for $C_{18}H_{15}N_4OS$ $[M]^+$ 335.0967, found 335.0967; elemental analysis calcd. (%) for $C_{18}H_{14}N_4OS$: C 64.65, H 4.22, N 16.75; found: C 64.78, H 4.16, N 16.62.

2-(3-Methyl-2-thioxo-2,3-dihydro-1*H*-imidazol-1-yl)quinazolin-4(3*H*)-one (17b): A sample of the betaine **13b** (113 mg, 0.5 mmol) was used. The tione **17b** was obtained as brown solid. Yield 0.53 g, 41 %, m.p. > 260 °C (dec.). ^{1}H NMR (600 MHz, [D$_6$]DMSO): δ = 3.57 (s, 3H, H6′), 7.49 (d, ^1J = 2.6 Hz, 1H, H4′), 7.56–7.52 (m, 1H, H6, H6), 7.67 (d, ^1J = 8.1 Hz, 1H, H8), 7.90–7.81 (m, 1H, H6) 7.96 (d, ^1J = 2.6 Hz, 1H, H5′), 8.15 (dd, ^1J = 7.9 Hz, ^2J = 1.1 Hz, 1H, H5), 14.13 (s, 1H, H3) ppm. ^{13}C NMR (151 MHz, [D$_6$]DMSO): δ = 34.47 (C6′), 114.83 (C5′), 120.75 (C4a), 120.98 (C4′), 126.30 (C5), 126.57 (C6), 126.93 (C8), 135.13 (C7), 143.64 (C2), 147.58 (C8a), 160.28 (C4), 160.95 (C2′) ppm. IR (ATR): $\tilde{\nu}$ = 3190, 3155, 3116, 3033, 2914, 2881, 1680, 1611, 1564, 1514, 1471, 1446, 1386, 1245, 1156, 1114, 763, 722, 699, 658, 632, 556, 511, 478 cm^{-1}. HRMS (ESI) *m/z* calcd. for $C_{12}H_{10}N_4OSNa$ $[M + Na]^+$ 281.0473, found 281.0470; elemental analysis calcd. (%) for $C_{12}H_{10}N_4OS$: C 55.80, H 3.90, N 21.69; found: C 55.62, H 3.63, N 21.45.

2-(3-Butyl-2-thioxo-2,3-dihydro-1*H*-imidazol-1-yl)quinazolin-4(3*H*)-one (17c): A sample of the betaine **13c** (134 mg, 0.5 mmol) was used. The tione **17c** was obtained as brown solid. Yield 0.108 g, 72 %, m.p. 172 °C. ^{1}H NMR (600 MHz, [D$_6$]DMSO): δ = 0.93 (t, ^1J = 7.4 Hz, 3H, H9′), 1.38–1.28 (m, 2H, H8′), 1.77–1.69 (m, 2H, H7′), 4.05 (t, ^1J = 7.3 Hz, 2H, H6′), 7.56–7.50 (m, 2H, H4′, H6), 7.67 (d, ^1J = 8.1 Hz, 1H, H8), 7.86 (t, ^1J = 7.6 Hz, 1H, H7), 7.96 (d, ^1J = 2.6 Hz, 1H, H5′), 8.14 (d, ^1J = 7.2 Hz, 1H, H5), 14.11 (s, 1H, H3) ppm. ^{13}C NMR (151 MHz, [D$_6$]DMSO): δ = 13.52 (C9′), 19.11 (C8′), 29.71 (C7′), 46.44 (C6′), 115.22 (C5′), 119.98 (C4′), 120.77 (C4a), 126.28 (C5), 126.60 (C6), 126.95 (C8), 135.09 (C7), 143.70 (C2), 147.58 (C8a), 160.32 (C4), 160.49 (C2′) ppm. IR (ATR): $\tilde{\nu}$ = 3189, 3155, 3117, 2968, 2953, 2860, 1678, 1619, 1564, 1512, 1455, 1398, 1248, 1149, 766, 725, 703, 661, 630, 532 cm^{-1}. HRMS (ESI) *m/z* calcd. for $C_{15}H_{16}N_4OSNa$ $[M + Na]^+$ 323.0943, found 323.0937; elemental analysis calcd. (%) for $C_{15}H_{16}N_4OS$: C 59.98, H 5.37, N 18.65; found: C 59.92, H 5.36, N 18.49.

2-(3-Allyl-2-thioxo-2,3-dihydro-1*H*-imidazol-1-yl)quinazolin-4(3*H*)-one (17d): A sample of the betaine **13d** (126 mg, 0.5 mmol) was used. The tione **17d** was obtained as brown solid. Yield 0.032 g, 22 %, m.p. > 155 °C (dec.). ^{1}H NMR (600 MHz, [D$_6$]DMSO): δ = 4.70 (d, ^1J = 5.5 Hz, 2H, H6′), 5.20 (dd, ^1J = 17.1 Hz, ^2J = 1.4 Hz, 1H, H8′), 5.28 (dd, ^1J = 10.3 Hz, ^2J = 1.3 Hz, 1H, H8′), 6.03–5.91 (m, 1H, H7′), 7.45 (d, ^1J = 2.7 Hz, 1H, H4′), 7.55 (t, ^1J = 7.1 Hz, 1H, H6), 7.69 (d, ^1J = 7.9 Hz, 1H, H8), 7.91–7.83 (m, 1H, H7), 7.97 (d, ^1J = 2.7 Hz, 1H, H5′), 8.16 (dd, ^1J = 7.9 Hz, ^2J = 1.1 Hz, 1H, H5), 14.04 (s, 1H, H3) ppm. ^{13}C NMR (151 MHz, [D$_6$]DMSO): δ = 48.72 (C6′), 115.49 (C5′), 118.64 (C8′), 119.78 (C4′), 120.80 (C4a), 126.29 (C5), 126.68 (C6), 126.98 (C8), 131.46 (C7′), 135.12 (C7), 143.66 (C2), 147.56 (C8a), 160.37 (C4), 160.92 (C2′) ppm. IR (ATR): $\tilde{\nu}$ = 3197, 3154, 3040, 2881, 2832, 1679, 1622, 1563, 1516, 1412, 1392, 1247, 1147, 767, 723, 702, 627 cm^{-1}. HRMS (ESI) *m/z* calcd. for $C_{14}H_{12}N_4OSNa$ $[M + Na]^+$ 307.0630, found 307.0618.

2-(3-Benzyl-2-selenoxo-2,3-dihydro-1*H*-imidazol-1-yl)quinazolin-4(3*H*)-one (18a): A sample of the betaine **13a** (151 mg, 0.5 mmol) was used. The selenone **18a** was obtained as brown solid. Yield 0.092 g, 48 %, m.p. > 232 °C (dec.). ^{1}H NMR (600 MHz, [D$_6$]DMSO): δ = 5.41 (s, 2H, H6′), 7.35–7.32 (m, 1H, H10′), 7.41–7.38 (m, 2H, H9′), 7.44–7.41 (m, 2H, H8′), 7.61–7.57 (m, 1H, H6), 7.66 (d, ^1J = 2.5 Hz, 1H, H4′), 7.71 (d, ^1J = 7.9 Hz, 1H, H8), 7.91–7.85 (m, 1H, H7), 8.01 (d, ^1J = 2.5 Hz, 1H, H5′), 8.18 (dd, ^1J = 7.9 Hz, ^2J = 1.4 Hz, 1H, H5) 13.71 (s, 1H, H3) ppm. ^{13}C NMR (151 MHz, [D$_6$]DMSO): δ = 51.30 (C6′), 119.20 (C5′), 121.21 (C4a), 121.41 (C4′), 126.26 (C5), 127.22 (C6, C8), 127.93 (C8′, C10′), 128.60 (C9′), 135.02 (C7), 135.71 (C7′), 143.92 (C2), 147.52 (C8a), 155.30 (C2′), 161.22 (C4) ppm. ^{77}Se NMR (144 MHz, [D$_6$]DMSO): δ = 100.57 ppm. IR (ATR): $\tilde{\nu}$ = 3185, 3152, 3110, 3029, 2923, 2849, 2806, 1678, 1616, 1587, 1563, 1513, 1444, 1386, 1243, 1148, 1086, 795, 715, 701, 650, 630, 530, 461 cm^{-1}. HRMS (ESI) *m/z* calcd. for $C_{18}H_{14}N_4OSeNa$ $[M + Na]^+$ 405.0231, found 405.0221.

2-(3-Methyl-2-selenoxo-2,3-dihydro-1*H*-imidazol-1-yl)quinazolin-4(3*H*)-one (18b): A sample of the betaine **13b** (113 mg, 0.5 mmol) was used. The selenone **18b** was obtained as brown solid. Yield 0.070 g, 46 %, m.p. > 252 °C (dec.). ^{1}H NMR (600 MHz, [D$_6$]DMSO): δ = 3.66 (s, 3H, H6′), 7.57 (t, ^1J = 7.5 Hz, 1H, H6), 7.62 (d, ^1J = 2.1 Hz, 1H, H4′), 7.70 (d, ^1J = 8.1 Hz, 1H, H8), 7.87 (t, ^1J = 7.6 Hz, 1H, H7), 8.06 (d, ^1J = 2.1 Hz, 1H, H5′), 8.17 (d, ^1J = 7.9 Hz, 1H, H5), 13.88 (s, 1H, H3) ppm. ^{13}C NMR (151 MHz, [D$_6$]DMSO): δ = 36.30 (C6′), 117.85 (C5′), 120.94 (C4a), 122.44 (C4′), 126.18 (C5), 126.85 (C6), 127.01 (C8), 134.95 (C7), 143.48 (C2), 147.38 (C8a), 154.31 (C2′), 160.47 (C4) ppm. ^{77}Se NMR (114 MHz, [D$_6$]DMSO): δ = 120.85 ppm. IR (ATR): $\tilde{\nu}$ = 3198, 3165, 3042, 2877, 2829, 2765, 1687, 1615, 1586, 1564, 1519, 1445, 1370, 1320, 1254, 1152, 1111, 760, 729, 710, 646, 538, 468 cm^{-1}. HRMS (ESI) *m/z* calcd. for $C_{12}H_{10}N_4OSeNa$ $[M + Na]^+$ 328.9918, found 328.9909; elemental analysis calcd. (%) for $C_{12}H_{10}N_4OSe$: C 47.23, H 3.30, N 18.36; found: C 47.06, H 3.14, N 17.96.

2-(3-Butyl-2-selenoxo-2,3-dihydro-1*H*-imidazol-1-yl)quinazolin-4(3*H*)-one (18c): A sample of the betaine **13c** (151 mg, 0.5 mmol) was used. The selenone **18c** was obtained as brown solid. Yield 0.061 g, 35 %, m.p. 171 °C. ^{1}H NMR (600 MHz, [D$_6$]DMSO): δ = 0.94 (t, ^1J = 7.4 Hz, 3H, H9′), 1.38–1.30 (m, 2H, H8′), 1.80–1.72 (m, 2H, H7′), 4.13 (t, ^1J = 7.3 Hz, 2H, H6′), 7.61–7.56 (m, 1H, H6), 7.65 (d, ^1J = 2.5 Hz, 1H, H4′), 7.71 (d, ^1J = 7.7 Hz, 1H, H8), 7.88 (ddd, ^1J = 8.6 Hz, ^2J = 7.3 Hz, ^3J = 1.5 Hz, 1H, H7), 8.03 (d, ^1J = 2.5 Hz, 1H, H5′), 8.17 (dd, ^1J = 7.9 Hz, ^2J = 1.1 Hz, 1H, H5), 13.80 (s, 1H, H3) ppm. ^{13}C NMR (151 MHz, [D$_6$]DMSO): δ = 13.55 (C9′), 19.08 (C8′), 30.04 (C7′), 48.26 (C6′), 118.55 (C5′), 121.14 (C4a), 121.49 (C4′), 126.28 (C5), 127.13 (C6), 127.21 (C8), 135.08 (C7), 143.70 (C2), 147.50 (C8a), 153.89

(C2′), 160.81 (C4) ppm. ^{77}Se NMR (144 MHz, [D$_6$]DMSO): δ = 104.74 ppm. IR (ATR): $\tilde{\nu}$ = 3184, 3154, 3115, 2949, 2926, 2860, 2811, 1679, 1617, 1586, 1564, 1512, 1455, 1393, 1320, 1249, 1086, 796, 729, 702, 651, 628, 533, 462 cm^{-1}. HRMS (ESI) *m/z* calcd. for $C_{15}H_{16}N_4OSeNa$ [M + Na]$^+$ 371.0387, found 371.0404; elemental analysis calcd. (%) for $C_{15}H_{16}N_4OSe$: C 51.88, H 4.64, N 16.13; found: C 51.97, H 4.49, N 16.06.

2-(3-Allyl-2-selenoxo-2,3-dihydro-1*H*-imidazol-1-yl)quinazolin-4(3*H*)-one (18d): A sample of the betaine **13d** (151 mg, 0.5 mmol) was used. The selenone **18d** was obtained as brown solid. Yield 0.030 g, 18 %, m.p. 174 °C. ^{1}H NMR (600 MHz, [D$_6$]DMSO): δ = 4.79 (dt, ^1J = 5.5 Hz, ^2J = 1.4 Hz, 2H, H6′), 5.22 (dd, ^1J = 17.1 Hz, ^2J = 1.4 Hz, 1H, H8′), 5.30 (dd, ^1J = 10.3 Hz, ^2J = 1.4 Hz, 1H, H8′), 6.03–5.95 (m, 1H, H7′), 7.61–7.57 (m, 2H, H4′, H6), 7.71 (dd, ^1J = 8.1 Hz, ^2J = 0.5 Hz, 1H, H8), 7.91–7.86 (m, 1H, H7), 8.04 (d, ^1J = 2.5 Hz, 1H, H5′), 8.17 (dd, ^1J = 7.9 Hz, ^2J = 1.2 Hz, 1H, H5), 13.76 (s, 1H, H3) ppm. ^{13}C NMR (151 MHz, [D$_6$]DMSO): δ = 50.56 (C6′), 118.81 (C5′), 118.83 (C8′), 121.15 (C4a), 121.30 (C4′), 126.28 (C5), 127.18 (C6, C8), 131.57(C7′), 135.08 (C7), 143.72 (C2), 147.46 (C8a), 154.61 (C2′), 160.90 (C4) ppm. ^{77}Se NMR (144 MHz, [D$_6$]DMSO): δ = 103.43 ppm. IR (ATR): $\tilde{\nu}$ = 3176, 3142, 3101, 3021, 2871, 2853, 2809, 2750, 1679, 1617, 1586, 1564, 1504, 1452, 1385, 1317, 1248, 1084, 940, 759, 735, 699, 622, 531, 464 cm^{-1}. HRMS (ESI) *m/z* calcd. for $C_{14}H_{12}N_4OSeNa$ [M + Na]$^+$ 355.0074, found 355.0078.

General Procedure for the Synthesis of the Borane Adducts with BEt_3 (19a–d, 20c,d): Under an inert atmosphere a solution of 1.0 mmol of betaine and 2 equiv. excess of 1.0 M triethylborane in hexane (2 mL) in 20 mL of dry 1,4-dioxane was stirred at 200 °C for 10 h in a bomb tube. Then, the solvent was evaporated in vacuo. The resulting solid was purified by column chromatography (silica gel, elution gradient for **19a**–**d** petroleum ether → petroleum ether/ethyl acetate, 1:1, elution gradient for **20c**,**d** ethyl acetate → ethyl acetate/MeOH, 10:1).

1-Benzyl-12,12-diethyl-10-oxo-10,12-dihydro-1*H*-imidazo-[2′,1′:3,4][1,4,2]diazaborolo[5,1-*b*]quinazolin-4-ium-12-ide (19a): A sample of the betaine **13a** (302 mg, 1.0 mmol) was used. The resulting solid was purified by column chromatography (silica gel, petroleum ether/ethyl acetate, 1:1). The adduct **11a** was obtained as colorless solid. Yield 0.303 g, 82 %, m.p. > 244 °C (dec.). ^{1}H NMR (600 MHz, [D$_6$]DMSO): δ = 0.30 (t, ^1J = 7.7 Hz, 6H, H2″), 0.58 (dq, ^1J = 15.1 Hz, ^2J = 7.6 Hz, 2H, H1″), 1.04 (dq, ^1J = 15.3 Hz, ^1J = 7.7 Hz, 2H, H1″), 5.41 (s, 2H, H6′), 7.37–7.34 (m, 2H, H9′), 7.40–7.36 (m, 1H, H10′), 7.43 (m, 2H, H8′), 7.46 (t, ^1J = 7.5 Hz, 1H, H6), 7.63 (d, ^1J = 7.9 Hz, 1H, H8), 7.76 (t, ^1J = 7.6 Hz, 1H, H7), 7.89 (d, ^1J = 2.0 Hz, 1H, H4′), 8.12 (dd, ^1J = 7.9 Hz, ^2J = 1.2 Hz, 1H, H5), 8.24 (d, ^1J = 2.0 Hz, 1H, H5′) ppm. ^{13}C NMR (151 MHz, [D$_6$]DMSO): δ = 10.41 (C2″), 11.08 (br. s, C1″), 51.76 (C6′), 114.03 (C5′), 121.62 (C4a), 125.65 (C6), 125.99 (C8), 126.30 (C5), 126.64 (C4′), 127.66 (C8′), 128.44 (C10′), 128.86(C9′), 133.65 (C7), 135.23 (C7′), 148.02 (C2), 148.12 (C8a), 162.92 (C4), 172.69 (br. s, C2′) ppm. ^{11}B NMR (193 MHz, [D$_6$]DMSO): δ = –0.68 ppm. IR (ATR): $\tilde{\nu}$ = 3135, 2939, 2860, 2818, 1662, 1628, 1606, 1560, 1466, 1411, 1339, 1192, 1130, 1048, 1023, 940, 874, 764, 736, 713, 682 cm^{-1}. HRMS (ESI) *m/z* calcd. for $C_{22}H_{23}BN_4ONa$ [M + Na]$^+$ 393.1863, found 393.1858; elemental analysis calcd. (%) for $C_{22}H_{23}BN_4O$: C 71.37, H 6.26, N 15.13; found: C 71.24, H 6.31, N 15.06.

1-Methyl-12,12-diethyl-10-oxo-10,12-dihydro-1*H*-imidazo-[2′,1′:3,4][1,4,2]diazaborolo[5,1-*b*]quinazolin-4-ium-12-ide (19b): A sample of the betaine **13b** (226 mg, 1.0 mmol) was used. The resulting solid was purified by column chromatography (silica gel, petroleum ether/ethyl acetate, 1:1). The adduct **19b** was obtained as colorless solid. Yield 0.118 g, 40 %, m.p. 207 °C. ^{1}H NMR (600 MHz, [D$_6$]DMSO): δ = 0.41 (t, ^1J = 7.7 Hz, 6H, H2″), 0.68 (dq, ^1J = 15.2 Hz, ^2J = 7.7 Hz, 2H, H1″), 1.02 (dq, ^1J = 15.4 Hz, ^2J = 7.7 Hz, 2H, H1″), 3.86 (s, 3H, H6′), 7.45 (ddd, ^1J = 8.1 Hz, ^2J = 7.1 Hz, ^3J = 1.1 Hz, 1H, H6), 7.62 (dd, ^1J = 8.1 Hz, ^2J = 0.6 Hz, 1H, H8), 7.76 (ddd, ^1J = 8.6 Hz, ^2J = 7.1 Hz, ^3J = 1.6 Hz, 1H, H7), 7.79 (d, ^1J = 2.0 Hz, 1H, H4′), 8.12 (dd, ^1J = 7.9 Hz, ^2J = 1.2 Hz, 1H, H5), 8.16 (d, J = 2.0 Hz, 1H, H5′) ppm. ^{13}C NMR (151 MHz, [D$_6$][D$_6$]DMSO): δ = 10.63 (C2″), 10.72 (br. s, C1″), 35.27 (C6′), 113.44 (C5′), 121.62 (C4a), 125.59 (C6), 125.96 (C8), 126.30 (C5), 127.53 (C4′), 133.63 (C7), 148.04 (C2), 148.17 (C8a), 163.00 (C4), 172.43 (br. s, C2′) ppm. ^{11}B NMR (193 MHz, [D$_6$]DMSO): δ = –0.79 ppm. IR (ATR): $\tilde{\nu}$ = 3173, 2941, 2863, 2813, 1651, 1634, 1608, 1561, 1465, 1408, 1343, 1232, 1205, 1128, 942, 876, 777, 723, 679 cm^{-1}. HRMS (ESI) *m/z* calcd. for $C_{16}H_{19}BN_4ONa$ [M + Na]$^+$ 317.1550, found 317.1540; elemental analysis calcd. (%) for $C_{16}H_{19}BN_4O$: C 65.33, H 6.51, N 19.05; found: C 65.26, H 6.71, N 18.94.

1-Butyl-12,12-diethyl-10-oxo-10,12-dihydro-1*H*-imidazo-[2′,1′:3,4][1,4,2]diazaborolo[5,1-*b*]quinazolin-4-ium-12-ide (19c): A sample of the betaine **13c** (268 mg, 1.0 mmol) was used. The resulting solid was purified by column chromatography (silica gel, petroleum ether/ethyl acetate, 1:1). The adduct **19c** was obtained as colorless solid. Yield 0.135 g, 40 %, m.p. 115 °C. ^{1}H NMR (600 MHz, [D$_6$]DMSO): δ = 0.37 (t, ^1J = 7.7 Hz, 6H, H2″), 0.62 (dq, ^1J = 15.0 Hz, ^1J = 7.6 Hz, 2H, H1″), 0.93 (t, ^1J = 7.4 Hz, 3H, H9′), 1.08 (dq, ^1J = 15.3, ^2J = 7.7 Hz, 2H, H1″), 1.39–1.32 (m, 2H, H8′), 1.88–1.78 (m, 2H, H7′), 4.13 (t, ^1J = 7.4 Hz, 2H, H6′), 7.45 (t, ^1J = 7.5 Hz, 1H, H6), 7.62 (d, ^1J = 8.0 Hz, 1H, H8), 7.76 (t, ^1J = 7.6 Hz, 1H, H7), 7.91 (d, ^1J = 1.9 Hz, 1H, H4′), 8.12 (dd, ^1J = 7.9 Hz, ^2J = 1.1 Hz, 1H, H5), 8.20 (d, ^1J = 1.9 Hz, 1H, H5′) ppm. ^{13}C NMR (151 MHz, [D$_6$]DMSO): δ = 10.43 (C2″), 11.21 (br. s, C1″), 13.43 (C9′), 19.03 (C8′), 31.79 (C7′), 48.22 (C6′), 113.79 (C5′), 121.60 (C4a), 125.61 (C6), 125.96 (C8), 126.07 (C4′), 126.31 (C5), 133.65 (C7), 148.05 (C2), 148.16 (C8a), 162.95 (C4), 171.97 (br. s, C2′) ppm. ^{11}B NMR (193 MHz, [D$_6$]DMSO): δ = –0.64 ppm. IR (ATR): $\tilde{\nu}$ = 3103, 3078, 2939, 2865, 2822, 1660, 1631, 1608, 1558, 1472, 1429, 1416, 1343, 1133, 1024, 944, 796, 766, 687, 543 cm^{-1}. HRMS (ESI) *m/z* calcd. for $C_{19}H_{25}BN_4ONa$ [M + Na]$^+$ 359.2019, found 359.2014; elemental analysis calcd. (%) for $C_{19}H_{25}BN_4O$: C 67.87, H 7.49, N 16.66; found: C 68.07, H 7.45, N 16.61.

1-Allyl-12,12-diethyl-10-oxo-10,12-dihydro-1*H*-imidazo-[2′,1′:3,4][1,4,2]diazaborolo[5,1-*b*]quinazolin-4-ium-12-ide (19d): A sample of the betaine **13d** (252 mg, 1.0 mmol) was used. The resulting solid was purified by column chromatography (silica gel, petroleum ether/ethyl acetate, 1:1). The adduct **19d** was obtained as colorless solid. Yield 0.100 g, 31 %, m.p. 141 °C. ^{1}H NMR (600 MHz, [D$_6$]DMSO): δ = 0.37 (t, ^1J = 7.7 Hz, 6H, H2″) 0.63 (dq, ^1J = 15.2 Hz, ^2J = 7.7 Hz, 2H, H1″), 1.04 (dq, ^1J = 15.3 Hz, ^2J = 7.7 Hz, 2H, H1″), 4.81 (d, ^1J = 5.7 Hz, 2H, H6′), 5.26 (dd, ^1J = 17.1 Hz, ^2J = 1.1 Hz, 1H, H8′), 5.35 (dd, ^1J = 10.3 Hz, ^1J = 1.0 Hz, 1H, H8′), 6.07 (dq, ^1J = 10.7 Hz, ^2J = 5.7 Hz, 1H, H7′), 7.46 (t, ^1J = 7.5 Hz, 1H, H6), 7.63 (d, ^1J = 7.9 Hz, 1H, H8), 7.76 (t, ^1J = 7.2 Hz, 1H, H7), 7.82 (d, ^1J = 2.0 Hz, 1H, H4′), 8.12 (dd, ^1J = 7.9 Hz, ^2J = 1.3 Hz, 1H, H5), 8.22 (d, ^1J = 2.0 Hz, 1H, H5′) ppm. ^{13}C NMR (151 MHz, [D$_6$]DMSO): δ = 10.47 (C2″), 11.06 (br. s, C1″), 50.55 (C6′), 113.94 (C5′), 119.13 (C8′), 121.63 (C4a), 125.67 (C6), 126.00 (C8), 126.33 (C4′), 126.39 (C5), 132.28 (C7′), 133.69 (C7), 148.04 (C2), 148.16 (C8a), 162.99 (C4), 172.51 (br. s, C2′) ppm. ^{11}B NMR (193 MHz, [D$_6$]DMSO): δ = –1.01 ppm. IR (ATR): $\tilde{\nu}$ = 3129, 2931, 2861, 2814, 1632, 1604, 1559, 1469, 1412, 1335, 1194, 1127, 1048, 1023, 913, 873, 768, 738, 683, 545 cm^{-1}. HRMS (ESI) *m/z* calcd. for $C_{18}H_{21}BN_4ONa$ [M + Na]$^+$ 343.1706, found 343.1696; elemental analysis calcd. (%) for $C_{18}H_{21}BN_4O$: C 67.52, H 6.61, N 17.50; found: C 67.32, H 6.83, N 17.48.

10-Butyl-11,11-diethyl-5-oxo-10,11-dihydro-5*H*-imidazo-[2′,1′:3,4][1,4,2]diazaborolo[1,5-*a*]quinazolin-7-ium-11-ide (20c): A sample of the betaine **13c** (268 mg, 1.0 mmol) was used. The resulting solid was purified by column chromatography (silica gel, ethyl acetate/MeOH, 10:1). The adduct **20c** was obtained as colorless solid. Yield 0.037 g, 11 %, m.p. 172 °C. ^{1}H NMR (600 MHz, [D$_6$]DMSO): δ = 0.31 (t, ^1J = 7.7 Hz, 6H, H2″), 0.86–0.79 (m, 2H, H1″), 1.01–0.92 (m, 5H, H1″, H9′), 1.40–1.33 (m, 2H, H8′), 1.88–1.81 (m, 2H, H7′), 4.18 (t, ^1J = 7.4 Hz, 2H, H6′), 7.42 (t, ^1J = 7.4 Hz, 1H, H6), 7.65 (d, ^1J = 8.3 Hz, 1H, H8), 7.75 (t, ^1J = 7.7 Hz, 1H, H7), 7.92 (d, ^1J = 2.0 Hz, 1H, H4′), 8.12 (dd, ^1J = 7.9 Hz, ^2J = 1.3 Hz, 1H, H5), 8.20 (d, ^1J = 2.0 Hz, 1H, H5′) ppm. ^{13}C NMR (151 MHz, [D$_6$]DMSO): δ = 10.05 (C2″), 12.87 (br. s, C1″), 13.48 (C9′), 19.03 (C8′), 31.83 (C7′), 48.31 (C6′), 114.11 (C5′), 117.94 (C8), 119.81 (C4a), 124.60 (C6), 125.91 (C4′), 127.64 (C5), 133.62 (C7), 142.39 (C8a), 151.54 (C2), 169.58 (C4), 171.18 (br. s, C2′) ppm. ^{11}B NMR (193 MHz, [D$_6$]DMSO): δ = 0.19 ppm. IR (ATR): $\tilde{\nu}$ = 3098, 2935, 2860, 2821, 1645, 1598, 1542, 1479, 1443, 1415, 1377, 1330, 1123, 1016, 881, 763, 695, 532 cm^{-1}. HRMS (ESI) *m/z* calcd. for $C_{19}H_{25}BN_4ONa$ [M + Na]$^+$ 359.2019, found 359.2016; elemental analysis calcd. (%) for $C_{19}H_{25}BN_4O$: C 67.87, H 7.49, N 16.66; found: C 67.82, H 7.31, N 16.85.

10-Allyl-11,11-diethyl-5-oxo-10,11-dihydro-5*H*-imidazo-[2′,1′:3,4][1,4,2]diazaborolo[1,5-*a*]quinazolin-7-ium-11-ide (20d): A sample of the betaine **13d** (252 mg, 1.0 mmol) was used. The resulting solid was purified by column chromatography (silica gel, ethyl acetate/MeOH, 10:1). The Adduct **20d** was obtained as colorless solid. Yield 0.032 g, 10 %, m.p. 141 °C. ^{1}H NMR (600 MHz, [D$_6$]DMSO): δ = 0.30 (t, ^1J = 7.7 Hz, 6H, H2″), 0.87–0.80 (m, 2H, H1″), 0.97–0.90 (m, 2H, H1″), 4.86 (dt, ^1J = 5.6 Hz, ^2J = 1.4 Hz, 2H, H6′), 5.27 (dq, ^1J = 17.1 Hz, ^2J = 1.5 Hz, 1H, H8′), 5.36 (dq, ^1J = 10.3 Hz, ^2J = 1.2 Hz, 1H, H8′), 6.09 (ddt, ^1J = 17.1 Hz, ^2J = 10.4 Hz, ^3J = 5.6 Hz, 1H, H7′), 7.42 (ddd, ^1J = 8.0 Hz, ^2J = 7.2 Hz, ^3J = 1.0 Hz, 1H, H6), 7.64 (d, ^1J = 8.1 Hz, 1H, H8), 7.75 (ddd, ^1J = 8.6 Hz, ^2J = 7.1 Hz, ^3J = 1.6 Hz, 1H, H7),7.83 (d, ^1J = 2.0 Hz, 1H, H4′), 8.12 (dd, ^1J = 7.9 Hz, ^1J = 1.5 Hz, 1H, H5), 8.21 (d, ^1J = 2.0 Hz, 1H, H5′) ppm. ^{13}C NMR (151 MHz, [D$_6$]DMSO): δ = 10.09 (C2″), 10.12 (br. s, C1″), 50.61 (C6′), 114.21 (C5′), 117.98 (C8), 119.07 (C8′), 119.82 (C4a), 124.64 (C7), 126.32 (C4′), 127.65 (C5), 132.30 (C7′), 133.65 (C7), 142.41 (C8a), 151.54 (C2), 169.59 (C4), 171.60 (br. s, C2′) ppm. ^{11}B NMR (193 MHz, [D$_6$]DMSO): δ = 0.76 ppm. IR (ATR): $\tilde{\nu}$ = 3116, 2941, 2863, 2820, 1647, 1596, 1540, 1479, 1445, 1412, 1378, 1328, 1122, 1047, 915, 878, 765, 696, 540 cm^{-1}. HRMS (ESI) *m/z* calcd. for $C_{18}H_{21}BN_4ONa$ [M + Na]$^+$ 343.1706, found 343.1701; elemental analysis calcd. (%) for $C_{18}H_{21}BN_4O$: C 67.52, H 6.61, N 17.50; found: C 67.64, H 6.46, N 17.71.

General Procedure for the Synthesis of the Borane Adducts with BPh_3 (21a–d, 22c,d): Under an inert atmosphere a solution of 1.0 mmol of betaine and 2 equiv. excess of 0.25 M triphenylborane in THF (8 mL) in 20 mL of dry 1,4-dioxane was stirred at 200 °C for 20 h in a bomb tube. Then, the solvent was evaporated in vacuo. The resulting solid was purified by column chromatography (silica gel, elution gradient for **21a**–**d** petroleum ether → petroleum ether/ethyl acetate, 1:1, elution gradient for **22c**,**d** ethyl acetate → ethyl acetate/MeOH, 10:1).

1-Benzyl-10-oxo-12,12-diphenyl-10,12-dihydro-1*H*-imidazo-[2′,1′:3,4][1,4,2]diazaborolo[5,1-*b*]quinazolin-4-ium-12-ide (21a): A sample of the betaine **13a** (302 mg, 1.0 mmol) was used. The resulting solid was purified by column chromatography (silica gel, petroleum ether/ethyl acetate, 1:1). The adduct **21a** was obtained as colorless solid. Yield 0.326 g, 70 %, m.p. > 268 °C (dec.). ^{1}H NMR (600 MHz, [D$_6$]DMSO): δ = 5.16 (s, 2H, H6′), 6.69 (d, ^1J = 7.5 Hz, 2H, H8′), 7.14 (ddd, ^1J = 13.8 Hz, ^2J = 5.4 Hz, ^3J = 1.7 Hz, 2H, H9′), 7.20–7.15 (m, 6H, H3″, H4″), 7.22 (t, ^1J = 7.5 Hz, 1H, H10′), 7.35–7.30 (m, 4H, H2″), 7.46 (ddd, ^1J = 8.1 Hz, ^2J = 7.2 Hz, ^3J = 1.1 Hz, 1H, H6), 7.68 (d, ^1J = 8.1 Hz, 1H, H8), 7.74 (d, ^1J = 2.1 Hz, 1H, H4′), 7.78 (t, ^1J = 7.6 Hz, 1H, H7), 8.05 (d, ^1J = 7.9 Hz, 1H, H5), 8.32 (d, ^1J = 2.1 Hz, 1H, H5′) ppm. ^{13}C NMR (151 MHz, [D$_6$]DMSO): δ = 51.72 (C6′), 114.90 (C5′), 122.03 (C4a), 126.08 (C6), 126.15 (C4″), 126.20 (C8), 126.29 (C4′), 126.44 (C5), 127.35 (C3″), 128.17 (C8′), 128.41 (C10′), 128.57 (C9′), 133.73 (C2″), 133.98 (C7), 134.06 (C7′), 143.88 (C1″), 147.62 (C2), 147.70 (C8a), 162.27 (C4), 169.11 (C2′) ppm. ^{11}B NMR (193 MHz, [D$_6$]DMSO): δ = –2.50 ppm. IR (ATR): $\tilde{\nu}$ = 3147, 3087, 3002, 1671, 1640, 1609, 1556, 1468, 1415, 1359, 1189, 1118, 949, 876, 765, 694, 638 cm^{-1}. HRMS (ESI) *m/z* calcd. for $C_{30}H_{23}BN_4ONa$ [M + Na]$^+$ 489.1863, found 489.1859; elemental analysis calcd. (%) for $C_{30}H_{23}BN_4O$: C 77.27, H 4.97, N 12.01; found: C 77.18, H 5.00, N 11.86.

[3-^{15}N]-1-Benzyl-10-oxo-12,12-diphenyl-10,12-dihydro-1*H*-imidazo[2′,1′:3,4][1,4,2]diazaborolo[5,1-*b*]quinazolin-4-ium-12-ide (*21a): Synthesized as described for **21a**. Yield 0.336 g, 72 %, colorless solid, m.p. > 268 °C (dec.). ^{1}H NMR (600 MHz, [D$_6$]DMSO): δ = 5.16 (s, 2H, H6′), 6.69 (d, ^1J = 7.5 Hz, 2H, H8′), 7.14 (ddd, ^1J = 13.8 Hz, ^2J = 5.4 Hz, ^3J = 1.7 Hz, 2H, H9′), 7.20–7.15 (m, 6H, H3″, H4″), 7.22 (t, ^1J = 7.5 Hz, 1H, H10′), 7.35–7.30 (m, 4H, H2″), 7.46 (ddd, ^1J = 8.1 Hz, ^2J = 7.2 Hz, ^3J = 1.1 Hz, 1H, H6), 7.68 (d, ^1J = 8.1 Hz, 1H, H8), 7.74 (d, ^1J = 2.1 Hz, 1H, H4′), 7.78 (t, ^1J = 7.6 Hz, 1H, H7), 8.05 (d, ^1J = 7.9 Hz, 1H, H5), 8.32 (d, ^1J = 2.1 Hz, 1H, H5′) ppm. ^{13}C NMR (151 MHz, [D$_6$]DMSO): δ = 51.72 (C6′), 114.91 (C5′), 122.03 (d, ^2J = 5.1 Hz, C4a), 126.08 (C6), 126.15 (C4″), 126.20 (C8), 126.29 (C4′), 126.44 (C5), 127.35 (C3″), 128.17 (C8′), 128.41 (C10′), 128.57 (C9′), 133.73 (C2″), 133.98 (C7), 134.06 (C7′), 143.88 (C1″), 147.61 (d, ^1J = 11.9 Hz, C2), 147.70 (C8a), 162.26 (d, ^1J = 11.1 Hz, C4), 168.99 (C2′) ppm. ^{11}B NMR (193 MHz, [D$_6$]DMSO): δ = –2.50 ppm. IR (ATR): $\tilde{\nu}$ = 3147, 3087, 3002, 1671, 1640, 1609, 1556, 1468, 1415, 1359, 1189, 1118, 949, 876, 765, 694, 638 cm^{-1}. HRMS (ESI) *m/z* calcd. for $C_{30}H_{23}B^{15}NN_3ONa$ [M + Na]$^+$ 490.1833, found 490.1829.

1-Methyl-10-oxo-12,12-diphenyl-10,12-dihydro-1*H*-imidazo-[2′,1′:3,4][1,4,2]diazaborolo[5,1-*b*]quinazolin-4-ium-12-ide (21b): A sample of the betaine **13b** (226 mg, 1.0 mmol) was used. The resulting solid was purified by column chromatography (silica gel, petroleum ether/ethyl acetate, 1:1). The adduct **21b** was obtained as colorless solid. Yield 0.125 g, 32 %, m.p. > 303 °C (dec.). ^{1}H NMR (600 MHz, [D$_6$]DMSO): δ = 3.65 (s, 3H, H6′), 7.16–7.13 (m, 2H, H4″), 7.20–7.16 (m, 4H, H3″), 7.26 (dd, ^1J = 8.1 Hz, ^2J = 1.4 Hz, 4H, H2″), 7.46 (t, ^1J = 8.0 Hz, 1H, H6), 7.68 (d, ^1J = 7.6 Hz, 1H, H8), 7.78 (ddd, ^1J = 8.5 Hz, ^2J = 7.2 Hz, ^3J = 1.6 Hz, 1H, H7), 7.82 (d, ^1J = 2.0 Hz, 1H, H4′), 8.05 (dd, ^1J = 7.9 Hz, ^1J = 1.3 Hz, 1H, H5), 8.30 (d, ^1J = 2.0 Hz, 1H, H5′) ppm. ^{13}C NMR (151 MHz, [D$_6$]DMSO): δ = 35.50 (C6′), 113.93 (C5′), 122.00 (C4a), 126.02 (C4″), 126.03 (C6), 126.16 (C8), 126.43 (C5), 127.18 (C3″), 128.13 (C4′), 133.67 (C2″), 133.97 (C7), 143.75 (C1″), 147.66 (C2), 147.69 (C8a), 162.33 (C4), 168.94 (C2′) ppm. ^{11}B NMR (193 MHz, [D$_6$]DMSO): δ = –2.53 ppm. IR (ATR): $\tilde{\nu}$ = 3185, 3109, 3004, 1665, 1641, 1608, 1563, 1468, 1410, 1336, 1127, 875, 765, 700, 648 cm^{-1}. HRMS (ESI) *m/z* calcd. for $C_{24}H_{20}BN_4O$ [M]$^+$ 391.1730, found 391.1729; elemental analysis calcd. (%) for $C_{24}H_{19}BN_4O$: C 73.87, H 4.91, N 14.36; found: C 73.76, H 5.02, N 14.08.

[3-^{15}N]-1-Methyl-10-oxo-12,12-diphenyl-10,12-dihydro-1*H*-imidazo[2′,1′:3,4][1,4,2]diazaborolo[5,1-*b*]quinazolin-4-ium-12-ide (*21b): Synthesized as described for 21b. Yield 0.137 g, 35 %, colorless solid, m.p. > 303 °C (dec.). ^{1}H NMR (600 MHz, [D$_6$]DMSO): δ = 3.65 (s, 3H, H6′), 7.16–7.13 (m, 2H, H4″), 7.20–7.16 (m, 4H, H3″), 7.26 (dd, ^1J = 8.1 Hz, ^2J = 1.4 Hz, 4H, H2″), 7.46 (t, ^1J = 8.0 Hz, 1H, H6), 7.68 (d, ^1J = 7.8 Hz, 1H, H8), 7.78 (ddd, ^1J = 8.5 Hz, ^2J =

7.2 Hz, ^3J = 1.6 Hz, 1H, H7), 7.81 (d, ^1J = 2.0 Hz, 1H, H4′), 8.04 (dd, ^1J = 7.9 Hz, ^1J = 1.2 Hz, 1H, H5), 8.29 (d, ^1J = 2.0 Hz, 1H, H5′) ppm. ^{13}C NMR (151 MHz, [D$_6$]DMSO): δ = 35.52 (C6′), 113.96 (C5′), 122.01 (d, ^2J = 5.2 Hz, C4a), 126.05 (C4″), 126.08 (C6), 126.18 (C8), 126.46 (C5), 127.22 (C3″), 128.15 (C4′), 133.69 (C2″), 134.01 (C7), 143.77 (C1″), 147.67 (d, ^1J = 11.7 Hz, C2), 147.71 (C8a), 162.36 (d, ^1J = 11.1 Hz, C4), 168.97 (C2′) ppm. ^{11}B NMR (193 MHz, [D$_6$]DMSO): δ = –2.49 ppm. IR (ATR): $\tilde{\nu}$ = 3185, 3109, 3004, 1665, 1641, 1608, 1563, 1468, 1410, 1336, 1127, 875, 765, 700, 648 cm^{-1}. HRMS (ESI) *m/z* calcd. for $C_{24}H_{19}B^{15}NN_3ONa$ [M + Na]$^+$ 414.1520, found 414.1510.

1-Butyl-10-oxo-12,12-diphenyl-10,12-dihydro-1*H*-imidazo-[2′,1′:3,4][1,4,2]diazaborolo[5,1-*b*]quinazolin-4-ium-12-ide (21c): A sample of the betaine **13c** (268 mg, 1.0 mmol) was used. The resulting solid was purified by column chromatography (silica gel, petroleum ether/ethyl acetate, 1:1). The adduct **21c** was obtained as colorless solid. Yield 0.030 g, 7 %, m.p. > 244 °C (dec.). ^{1}H NMR (600 MHz, [D$_6$]DMSO): δ = 0.60 (t, ^1J = 7.4 Hz, 3H, H9′), 0.96–0.88 (m, 2H, H8′), 1.31–1.24 (m, 2H, H7′), 3.93 (t, ^1J = 7.6 Hz, 2H, H6′), 7.21–7.13 (m, 6H, H3″, H4″), 7.28–7.26 (m, 4H, H2″), 7.45 (t, ^1J = 7.5 Hz, 1H, H6), 7.68 (d, ^1J = 8.0 Hz, 1H, H8), 7.78 (t, ^1J = 7.6 Hz, 1H, H7), 0.60 (t, ^1J = 7.4 Hz, 1H, H4′), 8.03 (dd, ^1J = 7.9 Hz, ^2J = 1.0 Hz, 1H, H5), 8.34 (d, ^1J = 1.9 Hz, 1H, H5′) ppm. ^{13}C NMR (151 MHz, [D$_6$]DMSO): δ = 13.22 (C9′), 18.61 (C8′), 30.93 (C7′), 48.44 (C6′), 114.31 (C5′), 121.99 (C4a), 126.03 (C6), 126.06 (C4″), 126.17 (C8), 126.41 (C5), 126.56 (C4′), 127.20 (C3″), 133.61 (C2″), 133.96 (C7), 143.89 (C1″), 147.67 (C2), 147.73 (C8a), 162.22 (C4), 168.82 (C2′) ppm. ^{11}B NMR (193 MHz, [D$_6$]DMSO): δ = –2.41 ppm. IR (ATR): $\tilde{\nu}$ = 3211, 3156, 3116, 2934, 2867, 1728, 1668, 1637, 1556, 1487, 1469, 1431, 1328, 1234, 1108, 946, 874, 767, 704, 656 cm^{-1}. HRMS (ESI) *m/z* calcd. for $C_{27}H_{25}BN_4ONa$ [M + Na]$^+$ 455.2019, found 455.2021; elemental analysis calcd. (%) for $C_{27}H_{25}BN_4O$: C 75.01, H 5.83, N 12.96; found: C 74.94, H 5.77, N 12.82.

1-Allyl-10-oxo-12,12-diphenyl-10,12-dihydro-1*H*-imidazo-[2′,1′:3,4][1,4,2]diazaborolo[5,1-*b*]quinazolin-4-ium-12-ide (21d): A sample of the betaine **13d** (252 mg, 1.0 mmol) was used. The resulting solid was purified by column chromatography (silica gel, petroleum ether/ethyl acetate, 1:1). The adduct **22d** was obtained as colorless solid. Yield 0.100 g, 24 %, m.p. > 278 °C (dec.). ^{1}H-NMR (600 MHz, [D$_6$]DMSO): δ = 4.59 (d, ^1J = 6.1 Hz, 2H, H6′), 4.98 (dd, ^1J = 17.1 Hz, ^2J = 1.2 Hz, 1H, H8′), 5.08 (dd, ^1J = 10.3 Hz, ^2J = 1.0 Hz, 1H, H8′), 5.58 (ddt, ^1J = 16.3 Hz, ^2J = 10.3 Hz, ^3J = 6.1 Hz, 1H, H7′), 7.22–7.11 (m, 6H, H3″, H4″), 7.27 (dd, ^1J = 7.8 Hz, ^2J = 1.6 Hz, 4H, H2″), 7.46 (t, ^1J = 7.5 Hz, 1H, H6), 7.69 (d, ^1J = 7.6 Hz, 1H, H8), 7.79 (ddd, ^1J = 8.5 Hz, ^2J = 7.2 Hz, ^3J = 1.5 Hz, 1H, H7), 7.85 (d, ^1J = 2.1 Hz, 1H, H4′), 8.04 (dd, ^1J = 7.9 Hz, ^2J = 1.2 Hz, 1H, H5), 8.36 (d, ^1J = 2.0 Hz, 1H, H5′) ppm. ^{13}C NMR (151 MHz, [D$_6$]DMSO): δ = 50.52 (C6′), 114.63 (C5′), 120.27 (C8′), 122.00 (C4a), 126.07 (C6, C4″), 126.18 (C8), 126.43 (C5), 126.49 (C4′), 127.18 (C2″), 130.75 (C7′), 133.70 (C3″), 133.98 (C7), 143.78 (C1″), 147.62 (C2), 147.69 (C8a), 162.25 (C4), 169.05 (C2′) ppm. ^{11}B NMR (193 MHz, [D$_6$]DMSO): δ = –2.62 ppm. IR (ATR): $\tilde{\nu}$ = 3156, 3087, 3000, 1667, 1636, 1609, 1554, 1486, 1432, 1337, 1128, 944, 875, 768, 749, 708, 639 cm^{-1}. HRMS (ESI) *m/z* calcd. for $C_{26}H_{21}BN_4ONa$ [M + Na]$^+$ 439.1706, found 439.1697; elemental analysis calcd. (%) for $C_{26}H_{21}BN_4O$: C 75.02, H 5.08, N 13.46; found: C 74.99, H 5.06, N 13.29.

[3-^{15}N]-1-Allyl-10-oxo-12,12-diphenyl-10,12-dihydro-1*H*-imidazo[2′,1′:3,4][1,4,2]diazaborolo[5,1-*b*]quinazolin-4-ium-12-ide (*21d): Synthesized as described for **21d**. Yield 0.112 g, 27 %; colorless solid, m.p. > 278 °C (dec.). ^{1}H-NMR ([D$_6$]DMSO, 600 MHz): δ = 4.59 (d, ^1J = 6.1 Hz, 2H, H6′), 4.98 (dd, ^1J = 17.1 Hz, ^2J = 1.2 Hz, 1H, H8′), 5.07 (dd, ^1J = 10.3 Hz, ^2J = 1.0 Hz, 1H, H8′), 5.58 (ddt, ^1J = 16.3 Hz, ^2J = 10.3 Hz, ^3J = 6.1 Hz, 1H, H7′), 7.22–7.11 (m, 6H, H3″, H4″), 7.27 (dd, ^1J = 7.8 Hz, ^2J = 1.6 Hz, 4H, H2″), 7.46 (t, ^1J = 7.5 Hz, 1H, H6), 7.69 (d, ^1J = 7.6 Hz, 1H, H8), 7.79 (ddd, ^1J = 8.5 Hz, ^2J = 7.2 Hz, ^3J = 1.5 Hz, 1H, H7), 7.85 (d, ^1J = 2.1 Hz, 1H, H4′), 8.03 (dd, ^1J = 7.9 Hz, ^2J = 1.2 Hz, 1H, H5), 8.36 (d, ^1J = 2.0 Hz, 1H, H5′) ppm. ^{13}C-NMR (151 MHz, [D$_6$]DMSO): δ = 50.53 (C6′), 114.65 (C5′), 120.30 (C8′), 122.01 (d, ^2J = 4.7 Hz, C4a), 126.10 (C6, C4″), 126.20 (C8), 126.44 (C5), 126.51 (C4′), 127.20 (C2″), 130.77 (C7′), 133.71 (C3″), 134.01 (C7), 143.78 (C1″), 147.63 (d, ^1J = 11.6 Hz, C2), 147.70 (C8a), 162.26 (d, ^1J = 11.1 Hz, C4), 169.05 (C2′) ppm. ^{11}B-NMR ([D$_6$]DMSO, 193 MHz): δ = –1.80 ppm. IR (ATR): $\tilde{\nu}$ = 3156, 3087, 3000, 1667, 1636, 1609, 1554, 1486, 1432, 1337, 1128, 944, 875, 768, 749, 708, 639 cm^{-1}. HRMS (ESI) *m/z* calcd. for $C_{26}H_{21}B^{15}NN_3ONa^+$ [M + Na]$^+$ 440.1676, found 440.1664.

10-Butyl-5-oxo-11,11-diphenyl-10,11-dihydro-5*H*-imidazo-[2′,1′:3,4][1,4,2]diazaborolo[1,5-*a*]quinazolin-7-ium-11-ide (22c): A sample of the betaine **13c** (268 mg, 1.0 mmol) was used. The resulting solid was purified by column chromatography (silica gel, ethyl acetate/MeOH, 10:1). The adduct **22c** was obtained as colorless solid. Yield 0.065 g, 15 %, m.p. > 268 °C (dec.). ^{1}H NMR (600 MHz, [D$_6$]DMSO): δ = 0.62 (t, ^1J = 7.4 Hz, 3H, H9′), 1.03–0.96 (m, 2H, H8′), 1.39–1.32 (m, 2H, H7′), 3.93 (t, ^1J = 7.4 Hz, 2H, H6′), 7.12 (d, ^1J = 8.3 Hz, 1H, H8), 7.20 (t, ^1J = 7.2 Hz, 2H, H4″), 7.25 (t, ^1J = 7.3 Hz, 4H, H3″), 7.32–7.28 (m, 5H, H6, H2″), 7.45 (t, ^1J = 7.4 Hz, 1H, H7), 7.87 (d, ^1J = 2.0 Hz, 1H, H4′), 8.08 (dd, ^1J = 7.9 Hz, ^2J = 1.2 Hz, 1H, H5), 8.29 (d, ^1J = 2.0 Hz, 1H, H5′) ppm. ^{13}C NMR (151 MHz, [D$_6$]DMSO): δ = 13.07 (C9′), 18.56 (C8′), 30.82 (C7′), 48.38 (C6′), 114.29 (C5′), 119.35 (C8), 119.91 (C4a), 124.55 (C6), 126.42 (C4′), 126.68 (C4″), 127.39 (C5), 127.86 (C3″), 132.88 (C7), 133.39 (C2″), 141.69 (C8a), 142.27 (C1″), 151.53 (C2), 168.65 (C2′), 169.40 (C4) ppm. ^{11}B NMR (193 MHz, [D$_6$]DMSO): δ = –2.05 ppm. IR (ATR): $\tilde{\nu}$ = 3163, 3144, 3065, 2938, 1662, 1600, 1544, 1473, 1448, 1416, 1375, 1180, 1121, 1021, 979, 869, 793, 758, 711, 662, 596, 537 cm^{-1}. HRMS (ESI) *m/z* calcd. for $C_{27}H_{25}BN_4ONa$ [M + Na]$^+$ 455.2019, found 455.2015; elemental analysis calcd. (%) for $C_{27}H_{25}BN_4O$: C 75.01, H 5.83, N 12.96; found: C 74.92, H 5.86, N 12.82.

10-Allyl-5-oxo-11,11-diphenyl-10,11-dihydro-5*H*-imidazo-[2′,1′:3,4][1,4,2]diazaborolo[1,5-*a*]quinazolin-7-ium-11-ide (22d): A sample of the betaine **13d** (252 mg, 1.0 mmol) was used. The resulting solid was purified by column chromatography (silica gel, ethyl acetate/MeOH, 10:1). The adduct **22d** was obtained as colorless solid. Yield 0.080 g, 19 %, m.p. > 285 °C (dec.). ^{1}H NMR (600 MHz, [D$_6$]DMSO): δ = 4.59 (d, ^1J = 6.0 Hz, 2H, H6′), 4.98 (dd, ^1J = 17.1, ^2J = 1.1 Hz, 1H, H8′), 5.06 (dd, ^1J = 10.3, ^2J = 1.0 Hz, 1H, H8′), 5.63–5.56 (m, 1H, H7′), 7.13 (d, ^1J = 8.3 Hz, 1H, H8), 7.21–7.17 (m, 2H, H4″), 7.24 (t, ^1J = 7.3 Hz, 4H, H3″), 7.31–7.28 (m, 2H), 7.32–7.28 (m, 5H, H2″, H6), 7.45 (ddd, ^1J = 8.6 Hz, ^2J = 7.2 Hz, ^3J = 1.6 Hz, 1H, H7), 7.79 (d, ^1J = 2.0 Hz, 1H, H4′), 8.09 (dd, ^1J = 7.9 Hz, ^1J = 1.4 Hz, 1H, H8), 8.31 (d, ^1J = 2.0 Hz, 1H, H5′) ppm. ^{13}C NMR (151 MHz, [D$_6$]DMSO): δ = 50.55 (C6′), 114.72 (C5′), 119.40 (C8), 119.94 (C4a), 120.15 (C8″), 124.69 (C6), 126.35 (C4′), 126.77 (C4″), 127.47 (C5), 127.92 (C3″), 130.70 (C7′), 133.00 (C7), 133.59 (C2″), 141.80 (C8a), 142.23 (C1″), 151.57 (C2), 169.05 (C2′), 169.49 (C4) ppm. ^{11}B NMR (193 MHz, [D$_6$]DMSO): δ = –2.19 ppm. IR (ATR): $\tilde{\nu}$ = 3158, 3139, 3003, 1642, 1601, 1541, 1479, 1409, 1329, 1271, 1181, 984, 874, 768, 708, 632 cm^{-1}. HRMS (ESI) *m/z* calcd. for $C_{26}H_{21}BN_4ONa$ [M + Na]$^+$ 439.1706, found 439.1700; elemental analysis calcd. (%) for $C_{26}H_{21}BN_4O$: C 75.02, H 5.08, N 13.46; found: C 75.20, H 5.10, N 13.30.

[3-^{15}N]-10-Allyl-5-oxo-11,11-diphenyl-10,11-dihydro-5*H*-imidazo[2′,1′:3,4][1,4,2]diazaborolo[1,5-*a*]quinazolin-7-ium-11-ide (*22d): Synthesized as described for **22d**. Yield: 0.070 g, 17 %, colorless solid, m.p. > 285 °C (dec.). ^{1}H NMR (600 MHz, [D$_6$]DMSO): δ =

4.59 (d, ^1J = 6.0 Hz, 2H, H6′), 4.98 (dd, ^1J = 17.1 Hz, ^2J = 1.1 Hz, 1H, H8′), 5.06 (dd, ^1J = 10.3 Hz, ^2J = 1.0 Hz, 1H, H8′), 5.63–5.56 (m, 1H, H7′), 7.13 (d, ^1J = 8.3 Hz, 1H, H8), 7.21–7.17 (m, 2H, H4″), 7.24 (t, ^1J = 7.3 Hz, 4H, H3″), 7.31–7.28 (m, 2H), 7.32–7.28 (m, 5H, H2″, H6), 7.45 (ddd, ^1J = 8.6 Hz, ^2J = 7.2 Hz, ^3J = 1.6 Hz, 1H, H7), 7.79 (d, ^1J = 2.0 Hz, 1H, H4′), 8.09 (dd, ^1J = 7.9 Hz, ^1J = 1.4 Hz, 1H, H8), 8.30 (d, ^1J = 2.0 Hz, 1H, H5′) ppm. ^{13}C NMR (151 MHz, [D$_6$]DMSO): δ = 50.60 (C6′), 114.76 (C5′), 119.4 (C8), 119.96 (d, ^2J = 1.7 Hz, C4a), 120.21 (C8″), 124.76 (C6), 126.39 (C4′), 126.83 (C4″), 127.52 (C5), 127.97 (C3″), 130.73 (C7′), 133.07 (C7), 133.63 (C2″), 141.83 (C8a), 142.26 (C1″), 151.59 (d, ^1J = 6.6 Hz, C2), 169.08 (C2′), 169.57 (d, ^1J = 3.4 Hz, C4) ppm. ^{11}B NMR (193 MHz, [D$_6$]DMSO): δ = –2.31 ppm. IR (ATR): $\tilde{\nu}$ = 3158, 3139, 3003, 1642, 1601, 1541, 1479, 1409, 1329, 1271, 1181, 984, 874, 768, 708, 632 cm^{-1}. HRMS (ESI) *m/z* calcd. for $C_{26}H_{21}B^{15}NN_3ONa$ [M + Na]$^+$ 440.1676, found 440.1681.

General Procedure for the Synthesis of the Borane Adducts with Tris(pentafluorophenyl)borane B(C$_6$F$_5$)$_3$ (23a–c): Under an inert atmosphere a solution of 0.5 mmol of betaine and 2 equiv. excess of tris(pentafluorophenyl)borane B(C$_6$F$_5$)$_3$ (512 mg, 1.0 mmol) in 20 mL of dry 1,4-dioxane was stirred at r.t. for 5 h in a Schleck flask. Then, the solvent was evaporated in vacuo. The resulting solid was purified by column chromatography (silica gel, elution gradient petroleum ether → petroleum:ether/ethyl acetate, 1:2).

{[2-(1-Benzyl-1*H*-imidazol-3-ium-3-yl)quinazolin-4-yl]oxy}-tris(perfluorophenyl)borate (23a): A sample of the betaine **13a** (151 mg, 0.5 mmol) was used. The adduct **23a** was obtained as colorless solid. Yield 0.228 g, 56 %, m.p. >207 °C (dec.). ^{1}H NMR (600 MHz, [D$_6$]DMSO): δ = 5.50 (s, 2H, H6′), 7.43–7.39 (m, 3H, H9′, H10′), 7.50–7.48 (m, 2H, H8′), 7.70 (ddd, ^1J = 8.1 Hz, ^2J = 7.0 Hz, ^3J = 1.2 Hz, 1H, H6), 7.77 (t, ^1J = 1.8 Hz, 1H, H5′), 7.83 (dd, ^1J = 8.2 Hz, ^2J = 0.8 Hz, 1H, H8), 7.93 (t, ^1J = 1.9 Hz, 1H, H4′), 7.97 (ddd, ^1J = 8.3 Hz, ^2J = 6.9 Hz, ^3J = 1.5 Hz, 1H, H7), 8.25 (dd, ^1J = 8.2 Hz, ^2J = 1.4 Hz, 1H, H5), 9.83 (t, ^1J = 1.5 Hz, 1H, H2′) ppm. ^{13}C NMR (151 MHz, [D$_6$]DMSO): δ = 52.64 (C6′), 118.20 (C4a), 118.28 (C5′), 121.30 (br. s, C1″), 123.38 (C4′), 125.17 (C5), 126.43 (C8), 127.52 (C6), 128.69 (C8′), 128.85 (C10′), 128.92 (C9′), 133.91 (C7), 134.95 (C7′), 135.14 (C2′), 135.94 (dm, ^1J = 241.2 Hz, C2″), 138.26 (dm, ^1J = 244.5 Hz, C4″), 147.32 (dm, ^1J = 240.2 Hz, C3″), 148.42 (C2), 149.85 (C8a), 170.16 (C4) ppm. ^{11}B NMR (193 MHz, [D$_6$]DMSO): δ = –3.16 ppm. ^{19}F NMR (400 MHz, [D$_6$]DMSO): δ = –165.11 (t, ^1J = 20.2 Hz, 2F, F3″), –159.65 (t, ^1J = 21.7 Hz, 1F, F4″), –133.96 (d, ^1J = 22.2 Hz, 2F, F2″) ppm. IR (ATR): $\tilde{\nu}$ = 3674, 3176, 1644, 1595, 1514, 1447, 1381, 1275, 1080, 974, 931, 770, 747, 674, 624 cm^{-1}. HRMS (ESI) *m/z* calcd. for $C_{36}H_{13}BF_{15}N_4O$ [M]$^-$ 813.0948, found 813.0946; elemental analysis calcd. (%) for $C_{36}H_{14}BF_{15}N_4O$: C 53.10, H 1.73, N 6.88; found: C 52.98, H 1.79, N 6.68.

{[2-(1-Methyl-1*H*-imidazol-3-ium-3-yl)quinazolin-4-yl]oxy}tris-(perfluorophenyl)borate (23b): A sample of the betaine **13b** (113 mg, 0.5 mmol) was used. The adduct **23b** was obtained as colorless solid. Yield 0.177 g, 48 %, m.p. > 268 °C (dec.). ^{1}H NMR (600 MHz, [D$_6$]DMSO): δ = 3.92 (s, 3H, 6′), 7.68–7.72 (m, 2H, H6, H5′), 7.81–7.83 (m, 1H, H8), 7.85 (t, ^1J = 1.83 Hz, 1H, H4′), 7.97 (ddd, ^1J = 8.4 Hz, ^2J = 7.0 Hz, ^3J = 1.5 Hz, 1H, H7), 8.25 (dd, ^1J = 8.1 Hz, ^2J = 1.0 MHz, 1H, H5), 9.70 (s, 1H, H2′) ppm. ^{13}C NMR (151 MHz, [D$_6$]DMSO): δ = 36.39 (C6′), 117.42 (C5′), 118.2 (C4a), 121.2 (C1″), 124.62 (C4″), 125.20 (C5), 126.42 (C8), 127.50 (C6), 134.96 (C7), 135.82 (C2′), 136.00 (dm, ^1J = 251 Hz, C2″), 138.30 (dm, ^1J = 250 Hz, C4″), 147.40 (dm, ^1J = 242 Hz, C3″), 148.40 (C2), 149.90 (C8a), 170.21 (C4) ppm. ^{11}B NMR (193 MHz, [D$_6$]DMSO): δ = –3.29 ppm. ^{19}F NMR (400 MHz, [D$_6$]DMSO): δ = –165.16 (t, ^1J = 20.4 Hz, 2F, F3″), –159.60 (t, ^1J = 21.6 Hz, 1F, F4″), –133.97 (d, ^1J = 22.8 Hz, 2F, F2″) ppm. IR (ATR): $\tilde{\nu}$ = 3180, 1644, 1598, 1508, 1454, 1381, 1278, 1172, 1093, 975, 930, 871, 811, 772, 758, 693, 623 cm^{-1}. HRMS (ESI) *m/z* calcd. for $C_{30}H_9BF_{15}N_4O$ [M]$^-$ 737.0635, found 737.0645; elemental analysis calcd. (%) for $C_{30}H_{10}BF_{15}N_4O$: C 48.81, H 1.37, N 7.59; found: C 48.99, H 1.47, N 7.54.

{[2-(1-Methyl-1*H*-imidazol-3-ium-3-yl)quinazolin-4-yl]oxy}tris-(perfluorophenyl)borate (*23b): A sample of the betaine ***13b** (227 mg, 1.0 mmol) was used. The adduct ***23b** was obtained as colorless solid. Yield 0.166 g, 45 %, m.p. > 268 °C (dec.). ^{1}H NMR (600 MHz, [D$_6$]DMSO): δ = 3.92 (s, 3H, 6′), 7.73–7.68 (m, 2H, H6, H5′), 7.82 (d, ^1J = 8.3 Hz, 1H, H8), 7.85 (t, ^1J = 1.8 Hz, 1H, H4′), 7.97 (ddd, ^1J = 8.4 Hz, ^2J = 7.1 Hz, ^3J = 1.4 Hz, 1H, H7), 8.26 (dd, ^1J = 8.2 Hz, ^2J = 1.2 Hz, 1H, H5), 9.70 (s, 1H, H2′) ppm. ^{13}C NMR (151 MHz, [D$_6$]DMSO): δ = 36.39 (C6′), 117.41 (C5′), 118.17 (C4a), 121.26 (br. s, C1″), 124.62 (C4″), 125.18 (C5), 126.41 (C8), 127.50 (C6), 134.95 (C7), 135.83 (C2′), 135.99 (dm, ^1J = 248 Hz, C2″), 138.27 (dm, ^1J = 247 Hz, C4″), 147.35 (dm, ^1J = 241 Hz, C3″), 148.40 (d, ^1J = 5.9 Hz, C2), 149.87 (C8a), 170.2 (d, ^1J = 7.5 Hz, C4) ppm. ^{11}B NMR (193 MHz, [D$_6$]DMSO): δ = –3.61 ppm. ^{19}F NMR (400 MHz, [D$_6$]DMSO): δ = –165.16 (t, ^1J = 20.6 Hz, 2F, F3″), –159.60 (t, ^1J = 21.6 Hz, 1F, F4″), –134.00 (d, ^1J = 22.8 Hz, 2F, F2″) ppm. IR (ATR): $\tilde{\nu}$ = 3180, 1644, 1598, 1508, 1454, 1381, 1278, 1172, 1093, 975, 930, 871, 811, 772, 758, 693, 623 cm^{-1}. HRMS (ESI) *m/z* calcd. for $C_{30}H_9BF_{15}N_3{}^{15}NO$ [M]$^-$ 738.0606, found 738.0568.

{[2-(1-Butyl-1*H*-imidazol-3-ium-3-yl)quinazolin-4-yl]oxy}tris-(perfluorophenyl)borate (23c): A sample of the betaine **13c** (134 mg, 0.5 mmol) was used. The adduct **23c** was obtained as colorless solid. Yield 0.078 g, 20 %, m.p. > 247 °C (dec.). ^{1}H NMR (600 MHz, [D$_6$]DMSO): δ = 0.90 (t, ^1J = 7.4 Hz, 3H, H9′), 1.33–1.25 (m, 2H, H8′), 1.85–1.78 (m, 2H, H7′), 4.25 (t, ^1J = 7.2 Hz, 2H, H6′), 7.70 (t, ^1J = 7.6 Hz, 1H, H6), 7.77 (s, 1H, H5′), 7.83 (d, ^1J = 8.3 Hz, 1H, H8), 8.00–7.95 (m, 2H, H4′, H7), 8.26 (d, ^1J = 8.1 Hz, 1H, H5), 9.70 (s, 1H, H2′) ppm. ^{13}C NMR (151 MHz, [D$_6$]DMSO): δ = 13.24 (C9′), 18.79 (C8′), 31.01 (C7′), 49.35 (C6′), 117.83 (C5′), 118.19 (C4a), 121.16 (C1″), 123.38 (C4′), 125.19 (C5), 126.43 (C8), 127.52 (C6), 134.96 (C7), 135.07 (C2′), 135.91 (dm, ^1J = 253.6 Hz, C2″), 138.27 (dm, ^1J = 248.5 Hz, C4″), 147.34 (dm, ^1J = 245.6 Hz, C3″), 148.44 (C2), 149.87 (C8a), 170.19 (C4) ppm. ^{11}B NMR (193 MHz, [D$_6$]DMSO): δ = –4.21 ppm. ^{19}F NMR (400 MHz, [D$_6$]DMSO): δ = –165.14 (t, ^1J = 20.5 Hz, 2F, F3″) –159.65 (t, ^1J = 21.6 Hz, 1F, F4″), –133.98 (d, ^1J = 22.4 Hz, 1F, F2″) ppm. IR (ATR): $\tilde{\nu}$ = 3351, 3148, 2968, 1598, 1559, 1510, 1454, 1362, 1280, 1220, 1087, 977, 932, 814, 772, 756, 697, 674, 620 cm^{-1}. HRMS (ESI) *m/z* calcd. for $C_{33}H_{15}BF_{15}N_4O$ [M]$^-$ 779.1105, found 779.1108.

Acknowledgments

This work was supported by the Russian Ministry of Education and Science (State contract 4.6351.2017/8.9) and the Russian Foundation for Basic Research (grant 17-03-01029). Single crystal X-ray analysis of **23b** was performed at the User Facilities Centers of IGIC RAS within the State Assignment on Fundamental Research to the Kurnakov Institute of General and Inorganic Chemistry. We thank the Deutscher Akademischer Austauschdienst DAAD for the financial support of the internship of S. D. at Clausthal University of Technology, Germany.

Keywords: Anionic NHCs · Betaines · Boron compounds · Carbenes · Cyclic borates · Imidazol-2-ylidene

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Received: November 4, 2019